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EPDM Roofing

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Cleaning Aged EPDM Rubber Roofing Membrane Material for Patching: Laboratory Investigations and Recommendations

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Many U.S. Army installations are replacing old, low-slope built-up roofs using EPDM (ethylene-propylene-diene terpolymer) as the waterproofing component. EPDMs are nonpolar, relatively inert rubbers, and difficult to bond with adhesive. Unaddressed in prior studies, an important factor affecting seam performance and eventual patch durability is the surface condition of the aged EPDM rubber before bonding.

This study assessed the effectiveness of different cleaning methods for preparing aged EPDM membranes for patching, and recommends procedures for use in the field. Effectiveness of the cleaning methods was evaluated using tests of short-term strength and long-term creep rupture in peel. Several surface analytical techniques were also used (i.e., scanning electron microscopy, Fourier transform infrared spectroscopy, and contact angle measurement). A section of an aged, ballasted EPDM membrane, sampled from a roof after 10 years in service, was used in the study. Most of the methods evaluated were based on procedures currently used to prepare aged EPDM for patching.

It was concluded that aged EPDM can be cleaned adequately for patching, and a simple DMF "droplet test" may indicate the surface bonding condition accurately. Field evaluation of the DMF droplet test is recommended.

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13. ABSTRACT (Maximum 200 words) Many U.S. Army installations are replacing old, low-slope built-up roofs using EPDM (ethylene-propylene-diene terpolymer) as the waterproofing component. EPDMs are nonpolar, relatively inert rubbers, and difficult to bond with adhesive. Unaddressed in prior studies, an important factor affecting seam performance and eventual patch durability is the surface condition of the aged EPDM rubber before bonding. This study assessed the effectiveness of different cleaning methods for preparing aged EPDM membranes for patching, and recommends procedures for use in the field. Effectiveness of the cleaning methods was evaluated using tests of short-term strength and long-term creep rupture in peel. Several surface analytical techniques were also used (i.e., scanning electron microscopy, Fourier transform infrared spectroscopy, and contact angle measurement). A section of an aged, ballasted EPDM membrane, sampled from a roof after 10 years in service, was used in the study. Most of the methods evaluated were based on procedures currently used to prepare aged EPDM for patching. It was concluded that aged EPDM can be cleaned adequately for patching, and a simple DMF "droplet test" may indicate the surface bonding condition accurately. Field evaluation of the DMF droplet test is recommended.			
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EXECUTIVE SUMMARY

Introduction

The use of membranes made from vulcanized ethylene-propylene-diene terpolymer (EPDM) rubber as the waterproofing component of low-sloped roofing systems has become common in the United States. Some military installations are replacing many of their old, deteriorated, low-slope built-up roofs with EPDM roofing systems. EPDMs are essentially nonpolar, relatively inert rubbers. This makes the adhesive bonding of sheets difficult. A factor affecting seam performance that has not been addressed in studies to date is the condition of the surface of aged EPDM rubber before bonding to it. This factor is important because, as time passes, EPDM membranes in service may need patches or splices.

Since 1979, the U.S. Army Construction Engineering Research Laboratory (USACERL) has been field testing the performance of roofing systems such as EPDM as alternatives to built-up roofing (BUR). A key concern raised by this research is whether the surface characteristics of EPDM rubber are altered during weathering in such a way that successful bonding of the aged material becomes more difficult than with unaged rubber. To help address this question, a study was conducted to determine the effect of surface preparation on the surface characteristics of a cleaned sheet of aged EPDM rubber and the bond strength of seam specimens fabricated from it. This report presents the results of the study.

The laboratory research was carried out in two phases. In the preliminary phase, investigations were conducted on the use of analytical techniques for judging whether the surface of aged EPDM rubber has been properly cleaned before patches are bonded to it (Appendix A). The intent was to develop experimental procedures for EPDM rubber based on existing analytical methods. It was found that scanning electron microscopy (SEM), contact angle measurement, and Fourier transform infrared-attenuated total reflection (FTIR-ATR*) spectroscopy were useful for general laboratory analysis of EPDM rubber sheets.

In the main phase of the study, short- and long-term peel tests and the surface analytical techniques developed in the preliminary phase were used to determine the effectiveness of different methods for cleaning the surface of an aged EPDM membrane sample taken from a roof. The major laboratory tasks conducted were:

1. The surface of the uncleaned, aged EPDM sample was analyzed using the contact angle and FTIR procedures developed in the preliminary phase of the study.
2. The surface of the aged sample was cleaned using a variety of methods. Subsequently, the surfaces of the cleaned specimens were analyzed using the specified surface analysis procedures to characterize the effectiveness of the cleaning methods.
3. Seam specimens were prepared from the aged EPDM membrane material and cleaned using various methods; the bond strength of the seam specimens was measured as a function of the cleaning method using a T-Peel test.

* ATR is one of several varieties of FTIR spectroscopy. For purposes of brevity it is abbreviated as FTIR in this report. No other kind of infrared spectroscopy was used in this research.

4. The peel resistance of seam specimens made from the cleaned, aged EPDM membrane material under creep conditions was compared with that of specimens fabricated from new, well cleaned EPDM rubber.
5. The results of the bond strength measurements were compared to the surface cleanliness of the aged EPDM as determined by the specified surface analytical procedures. The strength measurements were rated as a function of the surface cleaning methods.

Experimental Materials and Methodology

The sample of aged EPDM membrane used in the cleaning experiments was cut from a ballasted roof system located in the mid-Atlantic region of the United States. It was a single sheet, about 10 years old, and had been covered with a talc-like release agent on both surfaces when manufactured. When the sheet was removed from the roof it was completely covered with a layer of dirt.

The procedure selected to clean the surface of the aged EPDM membrane material was based on use of the abrasion test apparatus described in ASTM* D 4213, *Standard Test Method for Wet Abrasion Resistance of Interior Paints*. The intent was to have a mechanical method for repeatedly scrubbing a brush or wiping a cloth in a reproducible manner across the surface of the EPDM sample. A cycle consisted of one back-and-forth stroke of the abrader across the sample. Two types of abraders were used: (1) a synthetic absorbent laboratory cleaning cloth and (2) a brush with stiff nylon bristles. The cloth abrader was used when the cleaning agent was an organic solvent. The brush abrader was used when the cleaning agent was a water-based solution.

Samples of the aged EPDM sheet were cleaned using 16 different methods, 11 of which were similar to procedures normally used in the field. Four methods were experimental in that surface preparation agents were investigated to determine whether these products could modify the EPDM surface during cleaning and, thus, possibly enhance adhesion. Finally, the 16th method was a procedure of manual scrubbing and solvent wiping that has been found to be a suitable laboratory method for preparing the surface of new EPDM rubber.

Peel Test Results

In selecting a peel test as one measure of the effect of the various surface cleaning methods on the surface of an aged EPDM membrane, an adhesive tape was selected for preparation of joint specimens instead of a solvent-based adhesive. The uncleaned rubber would not bond to the tape. However, after removal of some surface contaminants, joint specimens having relatively low peel strengths could be formed with the tape.

The aged EPDM rubber was cleaned to varying degrees with heptane or 75 percent heptane/25 percent methyl ethyl ketone (MEK) solution by volume (or volume/volume [v/v]). The number of cleaning cycles was progressively doubled on adjacent areas of the membrane from 5 to 160. The effect of the number of cycles was visually apparent: the surfaces became noticeably cleaner where the number of cleaning cycles was greater. Also, the strength of the joints increased where the number of cleaning cycles was greater. The data analysis showed a linear relationship between strength and the log of the number of cycles over the range of cycles employed. Based on this experiment, the subsequent cleaning

* ASTM: American Society for Testing and Materials.

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tests were conducted at 80 cycles. This number of cleaning cycles produced a relatively high peel strength in a time that was experimentally practical.

The aged EPDM rubber sheet was subjected to each of the 16 surface cleaning methods. T-peel joints were made from the cleaned rubber using the adhesive tape (Appendix B). All cleaning methods provided aged EPDM rubber surfaces that formed taped joint specimens whose peel strengths were comparable to bonds formed between solvent-based adhesives and new EPDM rubber. However, statistically significant differences between some cleaning methods were found. EPDM prepared by wiping with heptane, a method similar to the common field procedure of cleaning with unleaded gasoline, gave average joint strengths among the highest of those measured. Their strengths were higher than those of joints prepared by cleaning the aged rubber with water-based methods. Short-term strength and creep-rupture joints, prepared by tape-bonding the surface of the heptane-cleaned aged EPDM to a surface of clean, new EPDM, failed at the interface between the tape and the new rubber.

Contact Angle Results

The contact angle between a liquid and a solid surface is a convenient measure of wettability; it is an indicator of the affinity of a liquid for a solid. Contact angle and wettability are inversely related: as one increases, the other decreases. The contact angle measurement is sensitive to the first 0.5-1 nm (5-10 Å) layer on a solid surface. Thus, its measure reflects the chemical composition of the very top layer of the surface. Contact angle measurements (and wettability parameters derived from them) were used to complement the peel strength analysis. The effects of the various cleaning cycles on the contact angles between the membrane material and two liquids—water and methylene iodide—were determined after cleaning the rubber either with heptane or the 75/25 solution of heptane/MEK.

The results of these contact angle measurements showed that the uncleaned, aged EPDM rubber was very wettable by methylene iodide (a relatively nonpolar liquid) and was not wettable by water (a highly polar liquid). Cleaning with heptane and the heptane/MEK solution substantially decreased the wettability by methylene iodide and increased the wettability by water. The contact angle for water on the rubber decreased with the first few cleaning cycles, but after removal of most of the contaminants by cleaning, the contact angle showed a slight increase. This was attributed to increased surface exposure of the less polar rubber. When measured using methylene iodide, there was an initial increase in contact angle with five cleaning cycles, after which the contact angle remained essentially constant. The results of this experiment supported the T-peel results for selecting the number of cycles to be used in cleaning according to the 16 methods included in this study.

The contact angles of methylene iodide and water were measured for the aged EPDM rubber after cleaning according to all 16 methods. The specimens for this experiment were the same as those used in the T-peel tests. No systematic relationships between contact angle and cleaning method were found. The contact angle for methylene iodide varied only slightly as a function of cleaning method. This result implied that a number of cleaning methods would provide surfaces with similar wettability characteristics for nonpolar solvent-based adhesives.

FTIR Spectroscopy Results

The surfaces of the aged EPDM rubber specimens cleaned according to the 16 methods were analyzed with FTIR spectroscopy. It was found that the technique could distinguish the uncleaned surfaces of aged EPDM from well cleaned ones. Only minor differences among the FTIR spectra were

observed. It was found that specimens cleaned with water and other polar solvents (and wiped with a dry cloth) had residual water on their surfaces. However, the FTIR technique could not resolve whether the surfaces of the cleaned rubber specimens had a talc-like release agent on them like the new specimens did.

Scanning Electron Microscopy Results

Cleaned surfaces of the aged EPDM rubber were subjected to SEM surface analysis. The most notable feature of the resulting photomicrographs was the presence of platelet particles indicating the presence of release agent on the surfaces of most of the specimens. Where these particles were visible, however, it was not possible by looking at the micrographs to tell whether the amount varied among specimens as a function of the cleaning method. Qualitatively, all of the micrographs appeared to be comparable. The presence of platelet particles was not surprising because the original rubber sheet had been coated with a release agent during its manufacture. The majority of the cleaning methods apparently removed the loose particles from the surface, but left behind those that were more strongly bonded to, or perhaps partially embedded in, the rubber surface.

Only in the cases of two cleaning methods involving relatively vigorous abrasion were the rubber surfaces observed to be essentially free of platelet particles. Nevertheless, although the rubber surfaces were cleaned essentially free of release agent, the peel strengths of the taped bonds were not significantly greater than those made on rubber that still contained release agent after being washed with heptane.

Comparison of the Results of the Different Test Methods

The peel strength data for the cleaned, aged rubber specimens were compared with the information produced by the surface analytical techniques to look for evidence of systematic relationships. None was found between any of the wettability parameters and peel strength. Moreover, the SEM technique was not able to distinguish a surface that produced a relatively high peel-strength seam from a surface that produced a relatively low peel-strength seam. Similarly, the FTIR technique could not differentiate between surfaces providing bonds of different strength.

However, using the number of cleaning cycles as a measure of surface cleanness, after initial cycling, increases in the peel strength were accompanied by increases in the water contact angle. Therefore, the water contact angle could be used to assess the bonding condition of the EPDM surface after cleaning. If substantial amounts of the loose surface contaminants have been removed from a sample of EPDM, the water contact angle on the cleaned rubber should be greater than 55 degrees. However, use of such a criterion is not practical for field use, because no method for accurately estimating the water contact angle on EPDM rubber in the field is currently available.

A method for estimating the cleanness of EPDM surfaces in the field (as indicated by contact angle) was investigated. It was known from the data obtained in the preliminary phase of the present study that the spreading of a drop of water increased as the level of contamination of new EPDM increased (Appendix A). In other words, if the EPDM was not well cleaned, the water contact angle would decrease more rapidly over time compared to that measured for water on a well cleaned EPDM surface. The decrease in contact angle over time would be observed as a spreading of the drop of water on the rubber. Thus, in the field, the rate of spreading, or the change in size of the drop on the rubber surface, could be estimated, and allowable limits for a given period of time could be prescribed.

Preliminary tests of the spreading of water on the cleaned EPDM specimens showed that water was not a suitable liquid for this technique. Specifically, using the size of the drop as an indicator, it was not possible to see the difference in the spreading of water on EPDM specimens as a function of the number of cleaning cycles. Consequently, other liquids were investigated.

Dimethyl formamide (DMF) was found to be sensitive to differences in surface condition resulting from the various cleaning cycles. Furthermore, drops of DMF placed on the surfaces of the specimens cleaned for 80 cycles using the various cleaning methods did not spread appreciably within 5 minutes. These results were confirmed qualitatively, remaining consistent for repeated tests.

Based on these limited data, it is suggested that a "droplet test," using the spreading of a DMF drop as described above, be used in the field experimentally as a simple test of the bonding condition of aged EPDM after cleaning. Such a test would require little skill and no costly equipment.

FOREWORD

This research was conducted for the U.S. Army Engineering and Housing Support Center (USAEHSC) under MIPR No. E87880293, "Investigation of Weathered EPDM," dated September 1988; and MIPR No. E87890347, E87890349, and E87890362, "EPDM Roofing," dated September 1989. The USAEHSC technical monitor was Mr. M. Smith, CEHSC-FB.

The work was performed by the National Institute of Standards and Technology (NIST) on contract to the Engineering and Materials Division (FM) of the Infrastructure Laboratory (FL), U.S. Army Construction Engineering Research Laboratories (USACERL). The USACERL principal investigator was Mr. David M. Bailey. Dr. Walter J. Rossiter Jr., Dr. Tinh Nguyen, Mr. W. Eric Byrd, Mr. James F. Seiler, Jr., and Dr. James A. Lechner are employees of NIST. Dr. Paul A. Howdysshell is Chief, CECER-FM. Dr. Michael J. O'Connor is Chief, CECER-FL. The USACERL technical editor was Gordon L. Cohen, Information Management Office.

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COL Daniel Waldo, Jr., is Commander and Director of USACERL, and Dr. L.R. Shaffer is Technical Director.

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CLEANING AGED EPDM RUBBER ROOFING MEMBRANE MATERIAL FOR PATCHING: LABORATORY INVESTIGATIONS AND RECOMMENDATIONS

1 INTRODUCTION

Background

Some U.S. Army installations are replacing many of their old, deteriorated, low-slope built-up roofs with various alternative roofing systems, the most frequently used of which is EPDM (ethylene-propylene-diene terpolymer). The use of vulcanized EPDM rubber for low-sloped roofing membranes has become common in the U.S. Current estimates indicate that more than 93 million square meters (1 billion square feet) are being applied annually.¹ Army use of EPDM has been increasing since the mid-1970s. In 1980 the U.S. Army Corps of Engineers (USACE) issued Corps of Engineers Guide Specification (CEGS) 07530, *Elastomeric Roofing (EPDM)*.²

EPDM consists of sheets of rubber, with or without reinforcement, that are unrolled on a roof and seamed together. EPDMs are essentially nonpolar, relatively inert rubbers, making the sheets difficult to bond with adhesives. Proper seam formation is a critical parameter associated with long-term performance of EPDM roofing systems.³ Several studies based on short-term bond strength tests and long-term creep-rupture tests have been conducted on EPDM systems to provide baseline data on the factors affecting seam performance.⁴ These laboratory studies have been conducted using seam specimens fabricated from new (unaged) EPDM rubber. One factor affecting seam performance that has not been addressed in studies to date is the condition of the surface of aged EPDM rubber before bonding to it. This factor is important because, as time passes, EPDM membranes in service may need to be patched.

Since 1979, the U.S. Army Construction Engineering Research Laboratories (USACERL) has been field testing the performance of roofing systems such as EPDM as alternatives to built-up roofing (BUR).⁵ A key concern raised by these investigations is whether the surface characteristics of EPDM rubber are altered during weathering in such a way that successful bonding of the aged material becomes more difficult than bonding to unaged rubber. For example, on an EPDM test roof at Fort Benning, GA, it was found that some repair patches delaminated within months after formation.⁶ Although failure in the Fort

¹ Sunil Kumar, "Roofing Megatrends: A Manufacturer's Perspective," in *Roofing, the Next Decade* (The Roofing Industry Educational Institute, Englewood, CO, 1990); William C. Cullen, "Project Pinpoint Analysis: Trends and Problems in Low-Slope Roofing, 1983-1988" (National Roofing Contractors Association (NRCA, April 1990), p 27.

² *Elastomeric Roofing (EPDM)*.

³ Jonathan W. Martin, Edward Embree, Paul E. Stutzman, and James A. Lechner, "Strength and Creep-Rupture Properties of Adhesive-Bonded EPDM Joints Stressed in Peel," Building Science Series 169 (National Institute of Standards and Technology [U.S.], Gaithersburg, MD, May 1990); Walter J. Rossiter, Jr., "Field Evaluation of the Quality of Newly Formed Adhesive-Bonded Seams of Single-Ply Membranes," in May, J.O., Ed., *Roofs and Roofing* (Ellis Horwood Ltd., Chichester, 1988), pp 273-288; Chester T. Chmiel, "History of EPDM Splice Adhesives," *EPDM Lap Adhesives: Past, Present, Future Use, and Performance* (U.S. Midwest Roofing Contractors Association, Kansas City, MO, October 1986), pp 4-9.

⁴ Hiroshi Watanabe and Walter J. Rossiter, Jr., "Effects of Adhesive Thickness, Open Time, and Surface Cleanness on the Peel Strength of Adhesive-Bonded Seams of EPDM Rubber Roofing Membrane," in *Roofing Research and Standards Development: 2nd Volume*, ASTM STP 1088, Wallace, T.J., and Walter J. Rossiter, eds. (ASTM, Philadelphia, 1990).

⁵ E. Marvin, G. Middleton, L. Eubanks, M. Rosenfield, J. Blair, and E. Lindow, *Evaluation of Alternative Reroofing Systems*, Interim Report (IR) M-263/ADA071578 (U.S. Army Construction Engineering Research Laboratory, [USACERL], June 1979).

⁶ David M. Bailey, Stuart D. Foltz, and Myer J. Rosenfield, *Long-Term Field Test Results of Experimental EPDM and PUF Roofing*, TR M-90/09 (USACERL, April 1990).

the Fort Benning example was largely due to the use of improper repair materials and patching techniques, it illustrates the need to develop a technical basis for creating standard methods for preparing the surfaces of weathered EPDM and assessing their suitability for bonding.

Objective

The objective of this study was to evaluate methods for cleaning and preparing the surface of aged EPDM rubber roofing membrane material for patching or repair, and to develop procedures for assuring the quality of bonded seams.

Approach

Laboratory research was conducted to provide the technical basis for determining whether the surface of aged rubber has been properly prepared before patches are applied. The research was carried out in two phases.

In the preliminary phase, investigations were conducted on the use of surface analytical techniques for judging whether the surface of aged EPDM rubber has been properly cleaned before patches are bonded to it.⁷ The intent was to develop experimental procedures applicable to EPDM rubber based on existing analytical methods. It was found that scanning electron microscopy (SEM), contact angle measurements, and Fourier transform infrared-attenuated total reflection (FTIR-ATR*) spectroscopy were useful for general laboratory analysis of EPDM rubber sheets. Experimental procedures for using these techniques were developed and used in the main phase of the study. The major findings from these investigations are summarized in Appendix A.

As part of the preliminary phase, a survey to obtain information on the performance of EPDM roofing at Army installations was performed. The results of the survey were described in a National Institute of Standards and Technology (NIST) report.⁸ In general, the report concluded that EPDM roofing has been performing satisfactorily on Army facilities. Few problems were reported for these facilities, but those mentioned involved seams. According to facility personnel, however, the seam problems were isolated.

In the main phase of the study, short- and long-term peel tests were used in conjunction with the surface analytical techniques to determine the effectiveness of different methods for removing surface contamination from an aged EPDM membrane sample taken from a roof. The major laboratory tasks conducted in this phase were:

- The surface of the uncleaned, aged EPDM sample was analyzed using the contact angle and FTIR procedures* developed in the preliminary phase of the study.

⁷ Walter J. Rossiter, Jr., and Tinh Nguyen. *Cleaning of Aged EPDM Roofing Membrane Material for Patching: Surface Analysis Techniques*, NISTIR 4525 (National Institute of Standards and Technology [NIST], February 1991).

* ATR is one of several varieties of FTIR spectroscopy. For purposes of brevity it is abbreviated as FTIR in this report. No other kind of infrared spectroscopy was used in this research.

⁸ Walter J. Rossiter, Jr., and James F. Seiler, Jr., *Results of a Survey of the Performance of EPDM Roofing at Army Facilities*, NISTIR 89-4085 (NIST, June 1989).

* A thick layer of dirt on the surface of the sample prevented SEM analysis due to concern about damaging the instrument.

- The surface of the aged sample was cleaned using a variety of methods. Subsequently, the surfaces of the cleaned specimens were analyzed using the specified surface analysis procedures to assess the effectiveness of the cleaning methods.
- Seam specimens were prepared from the cleaned, aged EPDM membrane material using various methods; the bond strength of the seam specimens was measured as a function of the cleaning method using a T-peel test.
- The peel resistance under creep conditions of seam specimens made from the cleaned aged EPDM membrane material was compared with that of specimens fabricated from new, well cleaned EPDM rubber.
- The results of the bond strength measurements were compared to the surface cleanliness of the aged EPDM as determined by the specified surface analytical procedures. The strength measurements were rated as a function of the surface cleaning methods.
- Based on the study results, guidelines for preparing aged EPDM membranes for bonding were developed, and a simple method for assessing surface cleanliness was tested and suggested for experimental use.

Mode of Technology Transfer

Information generated from this study will impact CEGS 07350, *Elastomeric Roofing (EPDM)*, and Technical Manual (TM) 5-617, *Inspection, Maintenance, and Repair of Roofing Systems*.

2 EXPERIMENTAL MATERIALS AND METHODOLOGY

Materials

Aged EPDM Membrane Material

The sample of aged EPDM membrane used in the cleaning experiments was cut from a ballasted roof system located in the mid-Atlantic region of the United States.** It was a single sheet, about 3 x 3 m (10 x 10 ft), which had been in service about 10 years. The membrane material was nonreinforced, and during manufacture, had been covered on both surfaces with a talc-like release agent to prevent the rubber from sticking to itself during manufacturing. Table 1 gives the thickness and load-elongation data for the aged EPDM rubber sheet. The surface of the sheet was completely covered with a layer of dirt when removed from the roof. The sheet surface was not even, but contained dimples from its calendering.

To use this EPDM rubber sample for the evaluation of various cleaning methods, the original sheet was divided into two 3 x 1.5 m (10 x 5 ft) sections. Each section was labeled to distinguish it from the other, and further cut into smaller test samples measuring 170 x 400 mm (6 3/4 x 16 in.). The small test samples were numbered to allow for random sampling during subsequent cleaning and testing experiments.

New EPDM Membrane Material

New EPDM membrane material used in the preparation of seam specimens was of a type commercially available. It was nonreinforced and had a talc-like release agent on its surfaces. Table 1 includes thickness and load-elongation data for this sheet rubber. One surface of the sheet was cleaned by scrubbing with detergent and water, then rinsing with water, and finally drying in air at room temperature. Immediately before forming the seam specimens, the water-washed surface was cleaned by rubbing with a cloth soaked with reagent-grade heptane. This method had previously been shown to provide a well cleaned EPDM surface.⁹

Adhesive Tape

The adhesive tape used to make seam specimens was a commercially available butyl-based product for fabricating seams in EPDM roof membranes. The tape had a nominal thickness of 0.88 mm (0.035 in.). Both its surfaces were tacky, for direct application between the two EPDM sheets to be bonded. To prevent unwanted adhering of the tape to itself or other objects during shipping and handling, the surfaces were protected with release paper. In the laboratory, this paper was removed just before the tape was used to form joints.

** Plans for conducting the study included use of a membrane sample cut from an exposed (e.g., adhered) EPDM roofing system. Such a sample was obtained. However preliminary experiments in making seam specimens with adhesive tape indicated that bonds were readily formed with little preparation of the rubber surface. As a result, this exposed-membrane sample was not considered adequate for the planned experimentation and, consequently, the study focused on cleaning the dirt-covered EPDM sample obtained from the ballasted roof system.

⁹ Walter J. Rossiter, Jr., James F. Seiler, Jr., and Paul E. Stutzman, "Field Testing of Adhesive-Bonded Seams of Rubber Roofing Membranes," *Proceedings, 9th Conference on Roofing Technology* (NRCA, May 1989), pp 78-87.

Table 1
Properties of the EPDM Test Materials

Property	Units	EPDM Rubber Test Material	
		Aged	New
Nominal Thickness	mm (in.)	1.0 (0.04)	1.5 (0.06)
Stress at Break	MPa (lbf/in ²)	13.3 (1930)	10.7 (1550)
Elongation at break	percent	450	680
Modulus at 300% Elong.	MPa (lbf/in ²)	3.6 (520)	2.0 (290)

Note: The mechanical properties were determined according to the procedures given in ASTM D 412. The "aged" and "new" EPDM rubber materials were not of the same batch, but were distinctly different.

Cleaning Aged EPDM Membrane Material

Procedure

The procedure selected to clean the surface of the aged EPDM membrane material was based on use of the abrasion test apparatus described in ASTM D 4213, *Standard Test Method for Wet Abrasion Resistance of Interior Paints*.¹⁰ The intent was to have a mechanical method for repeatedly scrubbing a brush or wiping a cloth in a reproducible manner across the surface of the EPDM sample. Figure 1 shows the abrasion cleaning device with a brush placed on the surface of a dirty EPDM sample. The sample was held flat in place with vacuum suction. Note that the brush did not scrub the entire surface of the sample. Before putting the rubber sample into the cleaning device, the backside surface* was wiped thoroughly with a heptane-soaked cloth.

The size of each sample was 170 x 400 mm (6.75 x 16 in.). For safety reasons, when inflammable solvents were used as the cleaning agent, a motor driven by compressed air was used to cycle the abrader (i.e., brush or cloth) across the sample surface. A cycle consisted of one back-and-forth stroke of the abrader along the length of the sample. The average speed of the abrader was four cycles per minute.

¹⁰ ASTM D 4213-87, "Standard Test Method for Wet Abrasion Resistance of Interior Paints," *Annual Book of ASTM Standards*, Vol 06.01 (ASTM, 1989), pp 712-715.

* Although wiped thoroughly with solvent, for purposes of this report, the backside surface was called "uncleaned." This was done to distinguish it from the frontside surface, which was subjected to controlled cleaning using one of the 16 selected methods.

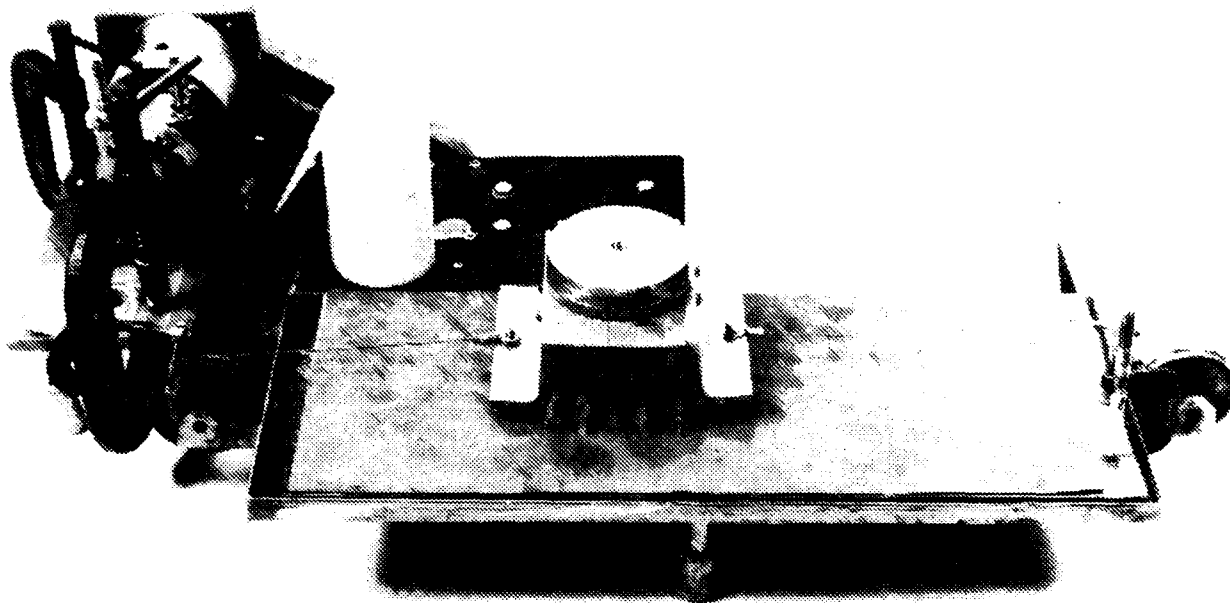


Figure 1. Abrasion Cleaning Device for EPDM Samples.

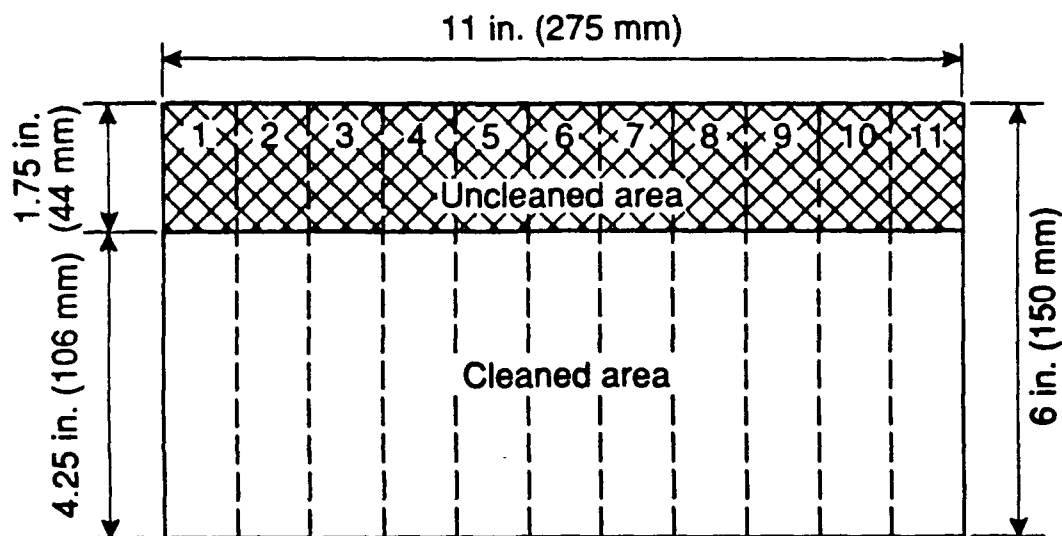
The contact area of the abrader surface with the sample surface measured 70 x 112 mm (2 3/4 x 4 1/2 in.). Two types of abraders could be clamped to the cleaning device: (1) a synthetic absorbent laboratory cleaning cloth and (2) a brush with stiff nylon bristles (Figure 1). In both cases, the mass of the abrader-clamp assembly was 1.1 kgm (2.5 lbm). Throughout cycling, the surface of the EPDM sample was kept wet with the cleaning agent, which was applied from a laboratory wash bottle. In general, over the course of an 80-cycle cleaning (i.e., the number used in most experiments), about 50 ml of a water-based detergent solution were used, or about 200 ml of organic solvents.

The cloth abrader was used when the primary cleaning agent was an organic solvent. A cloth was only used for 10 cycles after which it was replaced with another clean one.

The brush abrader was used when the primary cleaning agent was the water-based detergent. After every 10 cycles of cleaning, the brush was removed from the cleaning device and rinsed profusely (about 2 l in 15 seconds) under running tap water. After the device completed the desired number of cycles, the remaining detergent was removed from the sample surface. This was accomplished by two cycles of abrasion with a clean, dry cloth, followed immediately by two cycles with another cloth saturated with reagent-grade heptane.

Specimens for Testing and Analysis

A 150 x 275 mm (6 x 11 in.) section of the EPDM sample removed from the abrasion apparatus was cut so its cleaned surface area measured 106 x 275 mm (4.25 x 11 in.), as shown in Figure 2. The uncleaned portion of this section was used for handling and labeling. The section was divided into 11 strips, each with dimensions of 25 x 150 mm (1 x 6 in.). Four strips were randomly selected for peel tests, one was used for contact angle measurements, and another was used for FTIR spectroscopy and SEM observation.



Note: Strips were randomly selected for peel testing, contact angle measurement, FTIR spectroscopy, and SEM observation.

Figure 2. Sampling Pattern for Cleaned EPDM Specimen.

Surface Cleaning Methods

Table 2 summarizes some typical procedures used in the field to prepare the surface of aged EPDM rubber before patching. The summary was based on field experiences gained from sampling EPDM systems,¹¹ and from conversations with contractors experienced in installing EPDM roofing.¹² Most of the surface cleaning methods evaluated for effectiveness in this study were selected with consideration of the procedures described in Table 2.

Table 3 presents the 16 methods used to clean the aged EPDM samples. The first 11 methods were similar to typical procedures used in the field for cleaning aged EPDM rubber. Four methods (No. 1-4) used a cloth wipe with common solvents; five methods (No. 5-9) were based on brushing with water, with or without detergent; one method (No. 10) consisted of scrubbing followed by a solvent wipe; and another method (No. 11) employed a wire brush driven by an electric drill used with water and a detergent. Methods No. 12-15 involved experimental cleaning solutions and techniques. A proprietary silane coupling agent and a proprietary aromatic hydrocarbon tackifier, sometimes used in combination with heat, were investigated. The intent was to determine whether these products could modify an aged EPDM surface, while the surface was being cleaned, to enhance adhesion. Method No. 16 was a laboratory procedure using manual scrubbing action and solvent wiping of the surface. This method has been found to be a suitable laboratory method for preparing the surface of new EPDM rubber.¹³

¹¹ Walter J. Rossiter, Jr., James F. Seiler, William P. Spencer, James A. Lechner, and Paul E. Stutzman, "Characteristics of Adhesive-Bonded Seams Sampled From EPDM Roof Membranes," *Proceedings, 3rd International Symposium on Roofing Technology* (NRCA, 1991), pp 167-179; Walter J. Rossiter, Jr., James F. Seiler, William P. Spencer, James A. Lechner, and Paul E. Stutzman, "A Field Study of the Performance of EPDM Roofing at Air Force Facilities," NISTIR 4504 (NIST, 1990).

¹² Walter J. Rossiter, Jr., et al, June 1989.

¹³ Walter J. Rossiter, Jr., et al, May 1989.

Test Methods and Data Analysis

The four test methods (i.e., T-peel test, contact angle measurement, FTIR-ATR spectroscopy, and SEM analyses) used to evaluate the effectiveness of the 16 surface cleaning methods are described in Appendix B. Data were recorded in a computer file and analyzed using the graphics program Dataplot.¹⁴

Table 2
Typical Field Procedures for Cleaning Aged EPDM

Type of Cleaning	Procedure
<i>Solvent Wipe</i>	This is the most common; the procedure is akin to that used to form seams in the application of new EPDM membranes. An absorbent rag is soaked with unleaded gasoline or a similar solvent, and wiped on the surface to be patched. Some solvent may be poured on the membrane. As the rag becomes dirty, it is replaced with a clean one. Wiping is continued until the mechanic considers that the surface is adequately clean.
<i>Detergent Scrub Followed by Solvent Wipe</i>	This is often done when the roof has much a dirt on the surface. A detergent (often a household product) is added to water. The surface of the aged membrane is scrubbed by hand with the aqueous detergent solution using a stiff bristle brush. After drying, a solvent wipe is carried out.
<i>Detergent Scrub Followed by a Water Rinse and Solvent Wipe</i>	This is the same as the procedure above except that the scrubbed surface is rinsed with water before carrying out the solvent wipe. Rinsing is recommended by many contractors, but the extent to which it is done may depend on the availability of water on the roof. In some extreme cases, a water hose may be used.
<i>Mechanical Scrub Followed by a Water Rinse and Solvent Wipe</i>	This is essentially the same procedure as a that described above except that mechanical action such as an electrical floor scrubber is used. It is done less often than manual scrubbing, and may only be used if the contractor considers that an extensive area of the membrane surface is too dirty to clean by hand.

Table 3
The 16 Surface Cleaning Methods Used in This Study

Method No.	Type of Abrasion	No. of Cycles	Cleaning Solution ^a
1	Wipe	80	Reagent-grade heptane
2	Wipe	80	25% reagent-grade methyl ethyl ketone (MEK) in 75% reagent grade heptane (v/v)
3	Wipe	80	25% reagent-grade heptane in 75% reagent-grade MEK (v/v)
4	Wipe	80	Proprietary wash solution used for EPDM
5	Brush	80	Tap water without detergent ^b

^a Unless otherwise indicated, all steps were conducted at ambient temperatures (about 75 °F or 22 °C).

^b Samples cleaned with a method involving water were dried by two cycles of cloth abrasion using a clean dry cloth followed immediately by two cycles with a cloth saturated with heptane.

¹⁴ James J. Füllben, "Dataplot: An Interactive High-Level Language for Graphics, Non Linear Fitting, Data Analysis, and Mathematics," *Computer Graphics*, Vol 15 (1981), pp 199-213.

Table 3 (Cont'd)

Method No.	Type of Abrasion	No. of Cycles	Cleaning Solution
6	Brush	80	Tap water with household detergent #1
7	Brush	80	Tap water with household detergent #2
8	Brush	80	Tap water with household detergent #1; after every 10 cycles the rubber sample was rinsed under running tap water (flow of about 2L/min for 3 min.)
9	Brush	80	Tap water with a laboratory detergent
10	Brush/ Wipe	80	Tap water with household detergent #1 (40 cycles) followed by 25% MEK/75% heptane (40 cycles)
11	Electric Brush ^a	5	Tap water with household detergent #1; after scrubbing, the surface was wiped manually using a cloth soaked in heptane.
12	Wipe	80	Experimental cleaning agent #1: an aromatic hydrocarbon tackifier (2% by mass) and a silane coupling agent (2% by mass) in reagent-grade heptane; the silane was not soluble but dispersed.
13	Wipe	80	Reagent-grade heptane followed by experimental cleaning agent #2: a silane coupling agent (5% by mass) in ethyl alcohol was wiped on the surface of the rubber which was then heated in an oven at about 158 °F (70 °C) for 5 min.
14	Wipe	80	Experimental cleaning agent #3: an aromatic hydrocarbon tackifier (2% by mass) in heptane; a silane coupling agent (5% by mass) in ethyl alcohol was wiped on the surface of the rubber which was then heated in an oven at about 158 °F (70 °C) for 5 min.
15	Wipe	80	Experimental cleaning agent #4: a silane coupling agent (2% by mass) in water along with a laboratory detergent; the cleaned rubber was then heated in an oven at about 158 °F (70 °C) for 5 min.
16	Manual Brush/ Wipe	NA ^b	The sample was extensively scrubbed in a sink with a brush and detergent, rinsed under running tap water, and allowed to dry by setting on a laboratory bench overnight; this step was followed by wiping the dried surface with a cloth soaked with heptane.

^a Performed with a wire brush attached to an electric drill.

^b NA indicates not applicable.

3 RESULTS AND DISCUSSION

Peel Tests

The bond strength of a seam, as determined by the force required to separate a unit of the bonded area, is a useful criterion to assess the quality of the seam formation process. For EPDM roofing, the ultimate peel strength of seam specimens prepared from new rubber and solvent-based adhesive has been found to depend on the surface cleanness of the rubber sheet.¹⁵

Use of Tape for Specimen Joints

In selecting a peel test as one parameter for evaluating the various surface cleaning methods, it was necessary to fabricate joints for testing. In practice, solvent-based adhesives are the primary bonding agents for making seams, although in recent years, the use of tapes has increased.¹⁶ For the present study, solvent-based adhesives had a number of disadvantages that were overcome by use of tape:

- During application, the solvent in the adhesive might interact with the cleaned surface (in an unknown way) in such a way that effects attributable to the cleaning methods might not be observed.
- Control of application thickness of solvent-based adhesives—a difficult procedure—would be necessary because peel strength is affected by adhesive thickness.¹⁷ As a factory-produced material, tape can be assumed to have a relatively constant thickness.
- Butyl-based adhesives for EPDM roofing sheets tend to fail cohesively (rather than interfacially) in peel when the sheet surface is reasonably well cleaned.¹⁸ This factor raised the possibility that quantitative differences between some cleaning methods would be unobservable if they somehow acted to cause the cohesive failure of the test joint. Taped joints fail interfacially, however, eliminating the possibility of cohesive joint failure.

For these reasons, a tape was selected for preparing joint specimens. Using the joint specimen configuration shown in Figure B1, the specimens failed interfacially between the cleaned rubber surface and the tape. Preliminary experiments using new EPDM rubber cleaned by method No. 16 were conducted (data not shown) to determine the key parameters that needed to be controlled in the preparation of the specimens. Strength was found to depend on the pressure and the time over which it was applied during joint formation, and also the dwell time (i.e., time elapsed between joint formation and peel testing). Specimen preparation conditions were based, in part, on the results of the preliminary tests. Optimization of these three parameters was beyond the scope of this study. It was shown, however, that the strength of joint specimens having 7-day dwell time was not significantly different from those having a 4-day dwell time.

¹⁵ Jonathan W. Martin, et al., May 1990; Hiroshi Watanabe and Walter J. Rossiter, Jr.

¹⁶ Theresa O'Dea, "Sticking With EPDM Tapes," *Roofing/Siding/Insulation*, Vol 67, No. 9 (September 1990), pp 34-37.

¹⁷ Hiroshi Watanabe and Walter J. Rossiter, Jr., A.N. Gent, and G.G. Hamed, "Peel Mechanics of Adhesive Joints," *Polymer Engineering and Science*, Vol 19, No. 7 (1977), pp 462-466.

¹⁸ Jonathan W. Martin et al., May 1990; Hiroshi Watanabe and Walter J. Rossiter, Jr.

Preliminary Tests

In using the abrasion device described earlier for cleaning the surface of the aged EPDM sheet, it was necessary to set a criterion for judging the effectiveness of the cleaning method used. Two choices were apparent:

1. The number of cycles used in abrading the surface for a given cleaning method could vary. In this case, the criterion for assessing the effectiveness of the method would be the number of cycles at which the peel strength of the joint specimen reached a maximum. A low number of cycles would signify a more effective cleaning method.

2. The number of cycles used for all surface cleaning methods would be constant. In this case, the criterion for assessing the effectiveness of the cleaning method would be the peel strength achieved by the joint specimen. A high peel strength would signify a more effective cleaning method. This option was considered better in that the number of cycles involved in the cleaning method could be minimized.

To help choose between the two criteria, a preliminary experiment was conducted using the aged EPDM rubber specimen cleaned under methods No. 1 and 2. The number of cycles was progressively doubled from 5 to 160. Only one rubber sample was cleaned, but four joint specimens were prepared and peel-tested for each given number of cycles for each cleaning method.

The effect of increasing the number of cycles was visually apparent: as the number of cleaning cycles increased, the surfaces became noticeably cleaner (Figure 3).

The results for the preliminary experiment are given in Figure 4, where the peel strength of the joint specimens is plotted versus the number of cycles (Figure 4a) and the log of the number of cycles (Figure 4b). As is evident in these figures, joint strength increased as the number of cycles increased. No data are given for 0 cycles (i.e., the material as received from the roof) because the tape would not bond to the uncleaned EPDM surface. Statistical analysis of the data indicated that, for the total data set, there was no significant effect attributable to the cleaning method. As a consequence, only a single curve or line was fit to the data points in Figure 4. The data analysis showed a linear relationship between strength and the log of the number of cycles over the range of cycles employed. In general, each time the number

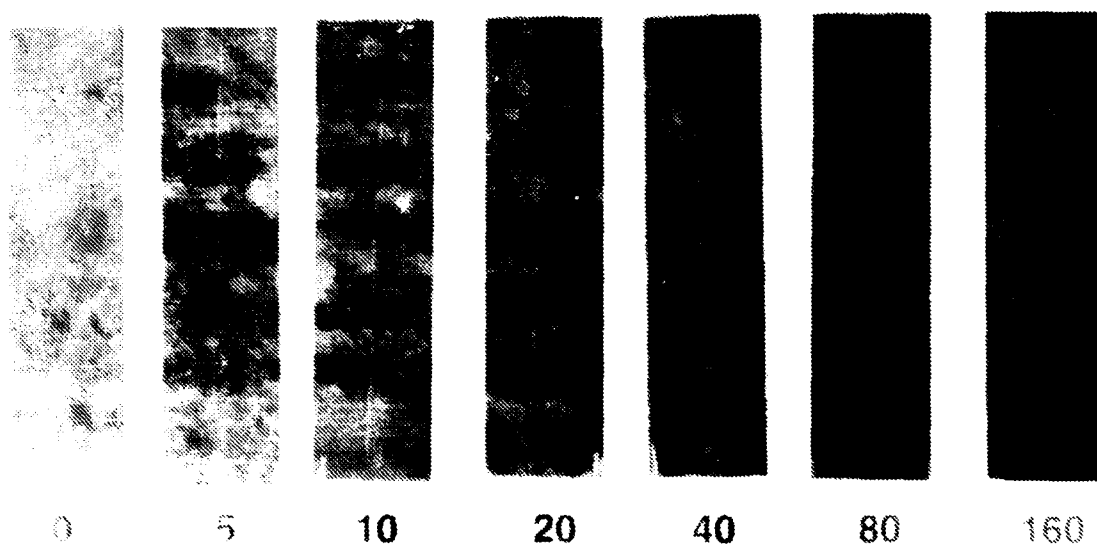


Figure 3. Surface Appearance of EPDM Specimens as a Function of Cleaning Cycles.

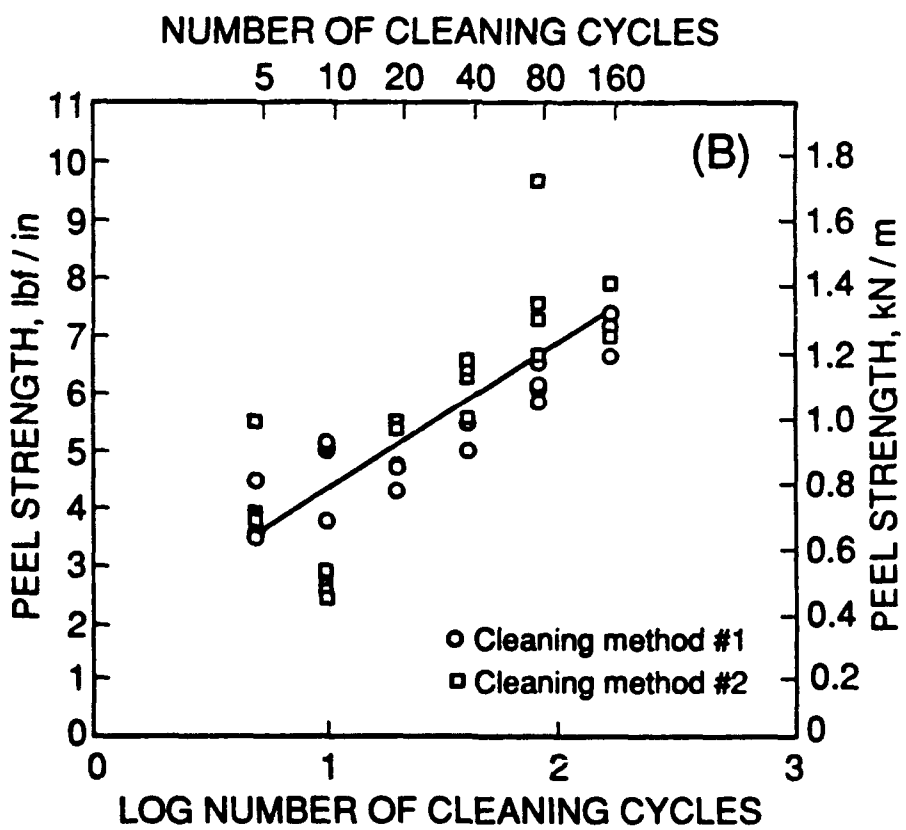
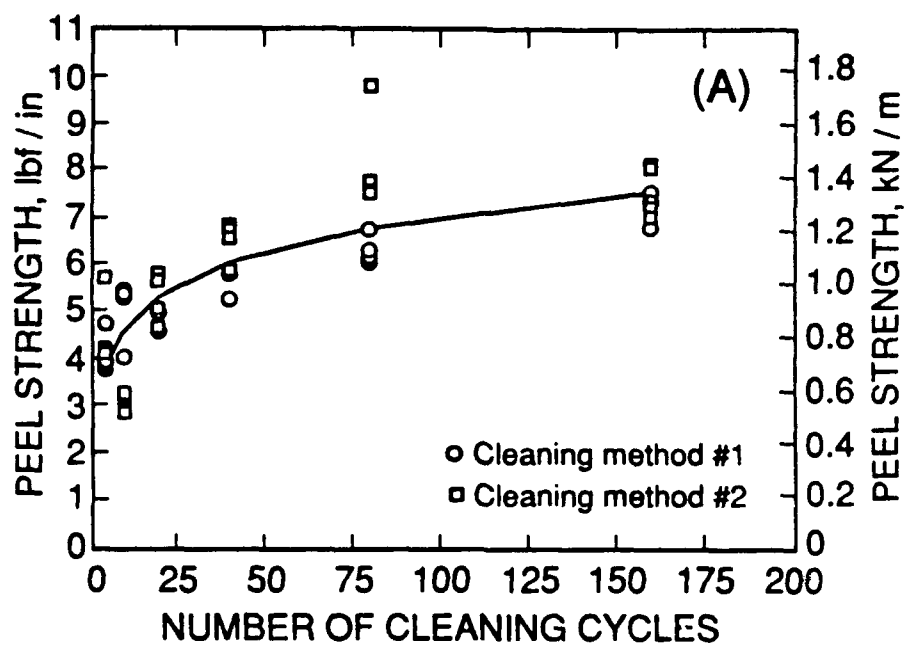


Figure 4. Peel Strength of Joint Specimens for Various Cleaning Methods.

of cycles was doubled, an incremental increase in strength of about 0.1 kN/m (0.8 lbf/in.) occurred. This finding suggested that cleaning at 320 cycles would further improve joint strength. This idea was not carried out, however, because given the cycling rate of the abrasion cleaning device (four cycles per minute), it was not practical to extend the cleaning to such large numbers of cycles.

Consequently, it was decided to conduct subsequent cleaning experiments at a constant number of cycles and judge effectiveness on the basis of the relative strength of each joint specimen. The number of cycles was set at 80 because the preliminary experiments showed that 80 cycles produced a relatively high peel strength in an experimentally reasonable time.

Cleaning Method Results

Two randomly sampled pieces of the aged EPDM rubber sheet were subjected to each of the surface cleaning methods given in Table 3. In turn, for each cleaned piece, a set of four replicate tape-joint specimens (Figure B1) was prepared for peel testing. The duplicate sets of peel specimens for a given cleaning method were assigned the designations "Set 1" and "Set 2." All Set 1 peel specimens were taken from one half of the large piece of EPDM rubber while the Set 2 peel specimens were sampled from the other half. The number of joint specimens studied was 128: two sets of four joints of each of the 16 cleaning methods.

The results of the peel strength measurements are given in Figure 5 for each set of tests for each cleaning method. An analysis of variance was performed on the data set, and indicated significant differences in peel strength among the various surface cleaning methods. Moreover, there were significant differences in strength between some sets for the same cleaning method. However, examination of the

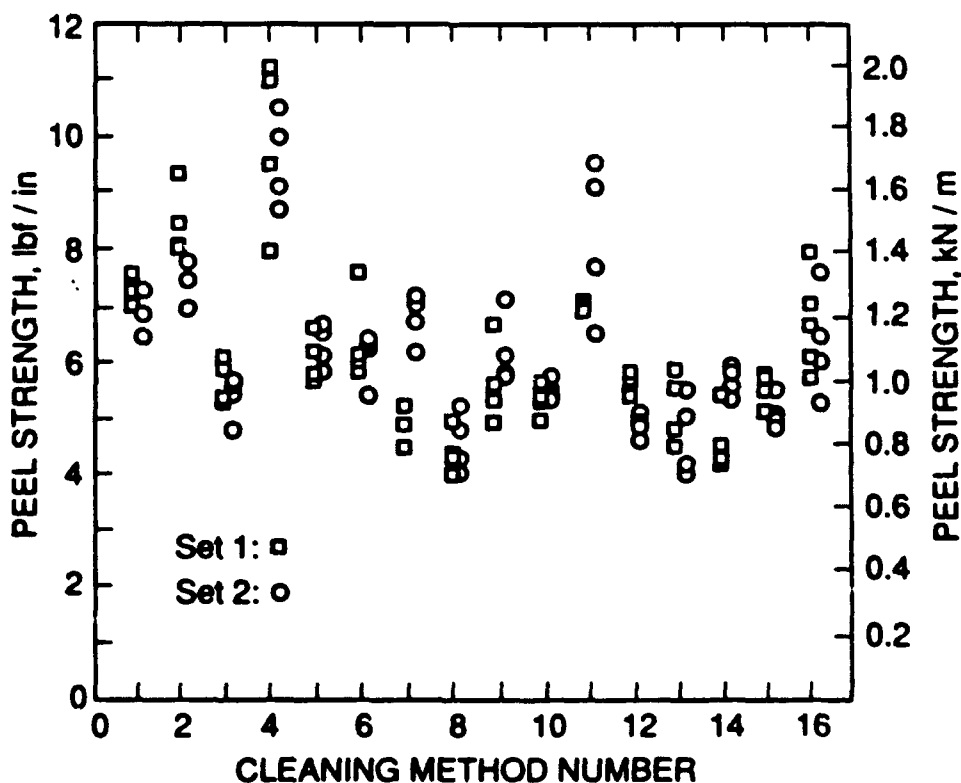


Figure 5. Peel Strength for Each Cleaning Method.

data uncovered no patterns. Therefore, the model proposed for further data analysis was that any given response (i.e., peel strength value) is the sum of three items:

1. An average (mean) strength characteristic of the cleaning method used
2. A random-effect characteristic of the particular set of peel specimens
3. A measurement error.

The mean strength values were assumed to be characteristic of the effectiveness of the various cleaning methods. The set effects and measurement error were assumed to be drawn randomly from distributions with means equal to zero so they could be characterized by the standard deviations of their respective distributions. Using this analysis model, conclusions were derived for the set effects and the cleaning method effects. Because all peel specimens in Set 1 were taken from one half of the original rubber sheet while those in Set 2 were taken from the other half, a consistent difference in the results for the two sets would indicate a difference between the two pieces of rubber. The analysis produced no evidence that there were any significant differences in the two pieces of rubber.

Table 4 gives the results of the analysis of the effects of the various surface cleaning methods. The average strength for all peel specimens for cleaning methods No. 2-15 are given and compared with the averages of cleaning methods No. 1 and 16, which were designated as controls. Method No. 1 (wiping the surface with a heptane solvent) was taken as a control because it is similar to the most common practice used in the field by roofing mechanics: wiping the EPDM surface with a cloth soaked with unleaded gasoline. Method No. 16 (scrubbing with detergent and water followed by a solvent wipe) was taken as a control because, as previously indicated, it was known to be effective for the laboratory preparation of the surface of new (unaged) EPDM rubber. No statistical difference in the average strengths of the peel specimens cleaned as controls was observed (Table 4).

The peel strengths of the tape-joint specimens ranged from 0.8 to 1.7 kN/m (4.6 to 9.8 lbf/in.), depending on the cleaning method used. This range of values was comparable to the peel strengths of field seams fabricated from solvent-based adhesives and new EPDM rubber.¹⁹

Only three of the surface cleaning methods (No. 2, 4, and 11) produced average peel strengths greater than the controls (Table 4). For methods No. 2 and 4 the difference was statistically significant; for method No. 11 it was not. Method No. 2 used a 75/25 solution of heptane/MEK. In this case, no practical significance was attributed to the higher strength, because the preliminary cycling experiment showed no overall difference between cleaning with heptane (method No. 1) and the 75/25 heptane/MEK solution (method No. 2). Method No. 4 used a proprietary wash solution. Its effect may have been due to the presence of bond-promoting agents in the solution (see "SEM Observations and Results," later in this chapter). Method No. 11 used a water-based detergent wash with a wire brush attached to an electric hand drill. Based on peel-strength measurements, mechanical abrasion with the wire brush prepared the surface more effectively than manual scrubbing followed by a solvent wipe (method No. 16), but it was not more effective than wiping with heptane alone (method No. 1).

As noted earlier, the surface of the aged EPDM sample, taken from a ballasted roof, was covered with a heavy layer of dirt. In planning the cleaning experiments, it was considered that washing with water-based detergent solutions might be an important step in surface cleaning. However, using peel strength as a benchmark, this was not found to be the case. As is evident in Table 4, with the exception

Table 4

Peel Strength of Joint Specimens for Various Cleaning Methods

Cleaning Method No.	Peel Strength			Comparison Versus Controls ^b			
	Average lb/in. kN/m	COV ^a %		Method #1 Diff. Sign.	Method #2 Diff. Sign.		
1-control	7.1	1.2	4.0	NA ^c	NA	+	No
2	7.9	1.4	6.5	+	Yes	+	Yes
3	5.6	1.0	7.0	-	Yes	-	Yes
4	9.8	1.7	12.6	+	Yes	+	Yes
5	6.2	1.1	6.5	-	Yes	-	No
6	6.3	1.1	10.6	-	Yes	o	No
7	5.9	1.0	6.3	-	Yes	-	No
8	4.6	0.8	9.9	-	Yes	-	Yes
9	6.0	1.1	11.6	-	Yes	-	No
10	5.4	0.9	4.1	-	Yes	-	Yes
11	7.2	1.3	12.0	+	No	+	Yes
12	5.3	0.9	3.8	-	Yes	-	Yes
13	5.0	0.9	13.6	-	Yes	-	Yes
14	5.1	0.9	9.0	-	Yes	-	Yes
15	5.3	0.9	5.6	-	Yes	-	Yes
16-control	6.3	1.1	11.3	-	No	NA	NA

^a Coefficient of variation for the combined peel data of Sets 1 and 2. It was calculated as the root mean square of the individual coefficients of variation for each set. This approach was taken because, in the case of some cleaning methods, significant differences were observed between the strengths of the Set 1 and Set 2 specimens.

^b The comparison was based on whether a difference (Diff.) was found between the average strength of a control and that for a given cleaning method. The symbol, o, indicates that no difference was found. The symbols, + and -, indicate whether an observed difference was an increase or a decrease, respectively, in average strength versus that of a control. Whether or not an observed difference was statistically significant (Sign.) at the 0.05 level is denoted by "Yes" and "No," respectively.

^c NA indicates "not applicable."

of method No. 11 versus method No. 16, none of the methods involving a water-based detergent solution (No. 5-11) produced higher bond strengths than the controls. In the case of methods No. 5-9, it might be assumed that the water-based procedure with only a little solvent wiping was biased toward removing the dirt and other polar contaminants from the surface, while leaving nonpolar and low-polarity contaminants. However, method No. 10 combined brushing with a water-based detergent followed by a wipe with the 75/25 heptane/MEK solution. This combination was not more efficient than wiping solely with heptane. One possible interpretation of these results is that residual water on the cleaned EPDM probably contributed to lowering the strength of the bond between the rubber sheet and the tape. This possibility was not investigated through further experiments for this study, although the FTIR analyses supported the hypothesis. (See "FTIR Spectroscopy Observations and Results" later in this chapter.)

The results of the methods using experimental cleaning agents (No. 12-15) are also noted in Table 4. The use of a proprietary aromatic tackifier or a proprietary silane coupling agent, either in the cleaning solvent or as an additional step to solvent cleaning, did not enhance bond strength. In fact, these four methods resulted in bond strengths that were among the lowest of those achieved.

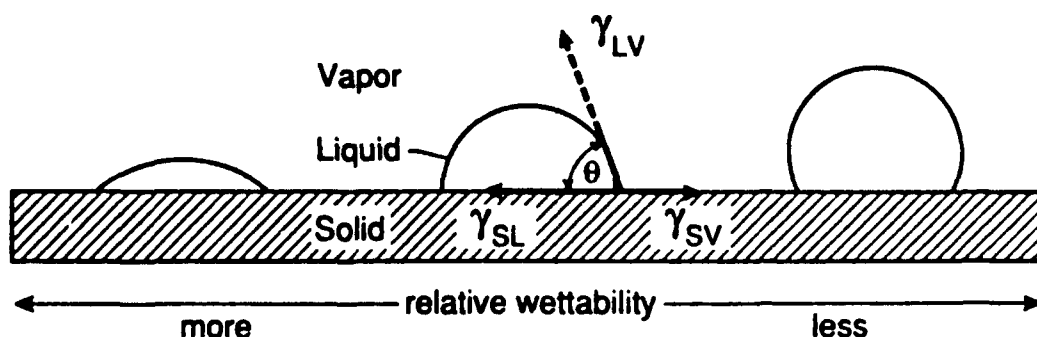
Contact Angle Measurements and Results

Background

The contact angle (Figure 6) of a liquid with a solid surface is a convenient measure of the affinity of a liquid for a solid (see Appendix B). This affinity is often referred to as wettability. Contact angle and wettability are inversely related: as one increases, the other decreases. A wide range of surface-sensitive techniques have been developed in the last decade to probe the surface characteristics of solids. Although extremely useful, many are sophisticated high-vacuum techniques, which are expensive, require highly skilled analysts, and are incompatible with liquids that are volatile in a vacuum. In contrast, contact angle measurements are relatively inexpensive and require less analytical skill. Furthermore, the contact angle measurement is sensitive to the top 0.5-1 nm (5-10 Å) of the solid surface. A layer of atomic thickness of a substance deposited on the surface of a test specimen may be adequate to change the wetting characteristics. Thus, the liquid's behavior reflects the chemical composition of the topmost atomic layers of the surface.

In addition to contact angle, the following wettability parameters used in the study were calculated from the contact angle measurements:

1. γ_s — This is the surface free energy (surface tension), the sum of γ_s^p and γ_s^d . The higher the value of γ_s , the more energetic (reactive) is the surface.
2. γ_s^p — This is the polar component of the surface free energy, and indicates the level of a surface's polarity. In comparing materials having the same γ_s , higher values of γ_s^p indicate surfaces of higher polarity.



Note: θ — contact angle; γ_{LV} — liquid/vapor interfacial tension; γ_{SV} — solid/vapor interfacial tension; γ_{SL} — solid/liquid interfacial tension.

Figure 6. Contact Angle and Interfacial Tensions for a Drop of Liquid Resting on a Solid Surface.

3. γ^d — This is the nonpolar (dispersion) component of the surface free energy that results from the interactions of the instantaneous dipole moments produced by molecules with or without a permanent dipole moment. This component signifies the nonpolar characteristics of a surface. For surfaces having the same γ_s , higher values of γ^d indicate surfaces of lower polarity. This component drops off more rapidly than γ^p as molecular distance between the adhesive and substrate increases. Thus, for example, in the case of adhesive bonding, substrates having only a γ^d component (i.e., no polar component) are normally more difficult to bond with an adhesive than those containing some level of polarity.

4. Polarity — This is the ratio between γ^p and γ^d , and measures the polar nature of the surface.

Effects of Cleaning Cycle on Contact Angle Measurements

Contact angle measurements were used to complement the peel strength analysis in the selection of a practical, effective number of cleaning cycles for evaluating the various surface cleaning methods. Thus, it was necessary to determine the effects of the cleaning cycle on the contact angles of two liquids (water and methylene iodide) placed on the aged EPDM rubber samples cleaned under methods No. 1 and 2 (Table 3). Four contact angles were measured for each cycle for each cleaning method, except for 0 (as received) and 80 cycles, where 8 and 12 measurements were taken, respectively.

Table 5 and Figures 7 and 8 present the effects of cleaning cycle on the contact angles and wettability parameters of water and methylene iodide on aged EPDM rubber cleaned by methods No. 1 and 2. For comparison, Table 5 also includes the results for specimens of aged and new EPDM rubber sheets cleaned by method No. 16.

The key results shown in Table 5 and Figures 7 and 8 are summarized below. Interpretation of the data follows the summary.

1. The uncleaned, aged EPDM rubber was very wettable by methylene iodide (a relatively nonpolar liquid) and was not wettable by water (a highly polar liquid).

2. Cleaning with heptane (method No. 1, a nonpolar solvent) and a 75/25 solution of heptane/MEK (method No. 2, a slightly polar solvent) decreased substantially the material's wettability by methylene iodide and increased its wettability by water.

3. After 5 cycles of cleaning method No. 1, wettability by methylene iodide remained essentially constant. In contrast, wettability by water increased (i.e., the contact angle decreased) up to 40 cycles; thereafter, wettability by water appeared to decrease.

4. For method No. 2, as the number of cleaning cycles increased to 40, wettability by methylene iodide decreased while wettability by water increased. Then both appeared to level off, except wettability by water increased at 160 cycles.

5. Increasing the number of method No. 1 cleaning cycles beyond 5 did not appear to affect the nonpolar component (γ^d) of the aged EPDM. However, its polar component (γ^p) and total surface free energy (γ_s) increased up to 40 cycles as a function of cleaning with the nonpolar heptane solvent, then appeared to decrease.

6. For cleaning method No. 2, the polar component increased and the nonpolar component decreased up to 40 cycles. Thereafter, the former increased while the latter decreased.

Table 5

**Contact Angles and Wettability Parameters for
Aged EPDM Rubber as a Function of Cleaning Cycles**

Cleaning Method	Cycles No.	Contact Angle ^b degrees		Surface Free Energy $\frac{\text{mJ/m}^2}$		Polarity	
		CH ₂ I ₂	H ₂ O	γ^d	γ^p	γ_s	γ^p/γ_s
NA ^c	0 ^d	8	98	63.3	0.8	64.1	0.01
1	5	48	65	23.2	16.6	39.8	0.42
1	10	49	73	25.5	10.9	36.4	0.30
1	20	48	60	21.1	21.7	42.8	0.51
1	40	47	47	17.3	34.5	51.8	0.67
1	80	51	50	16.1	33.0	49.1	0.67
1	160	48	64	22.4	18.2	40.6	0.45
2	5	29	95	52.1	0.0	52.1	0.00
2	10	36	97	48.3	0.0	48.3	0.00
2	20	40	65	27.5	14.8	42.3	0.35
2	40	51	56	17.8	26.8	44.5	0.60
2	80	50	62	20.6	20.6	41.2	0.50
2	160	53	39	12.1	46.0	58.0	0.79
16	NA	51	71	23.5	12.9	36.4	0.35
new EPDM rubber							
16	NA	52	75	24.3	10.4	34.7	0.30

^aData for well cleaned (Method No. 16) aged and new EPDM rubbers are included for purposes of comparison.

^bAverage of eight measurements; CH₂I₂ and H₂O indicate methylene iodide and water, respectively.

^cNA indicates not applicable.

^dThe measurements were conducted on the uncleaned aged EPDM.

7. For cleaning methods No. 1 and 2, the surface free energy values followed the polar component values as a function of cycles.

8. The cleaned, aged EPDM rubber was somewhat more polar than the cleaned, new rubber. (It should be noted that, since an unexposed sample of the aged EPDM was not available, it is not known whether this difference was due to formulation or aging effects.)

As an initial point of discussion, the contact angle data help characterize the contaminants on the surface of the aged EPDM rubber and how they behaved due to cleaning. The polar and nonpolar components and the polarity results indicate that the surface of the contaminants on the uncleaned, aged EPDM rubber was nonpolar. Note the polarity, which was essentially 0 (Table 5). This suggests that no polar sites were exposed on the uncleaned surface. The magnitude of the nonpolar component of the uncleaned, aged surface was much higher (63 mJ/m²) than that of organic compounds, which are generally nonpolar and have nonpolar components in the range of 18-40 mJ/m².²⁰ On the other hand, the nonpolar

²⁰ Souheng Wu, *Polymer Interface and Adhesion*, Section 14.7 (Marcel Dekker, New York, 1982); A.J. Kinloch, *Adhesion and Adhesives* (Chapman and Hall, New York, 1987), p 32.

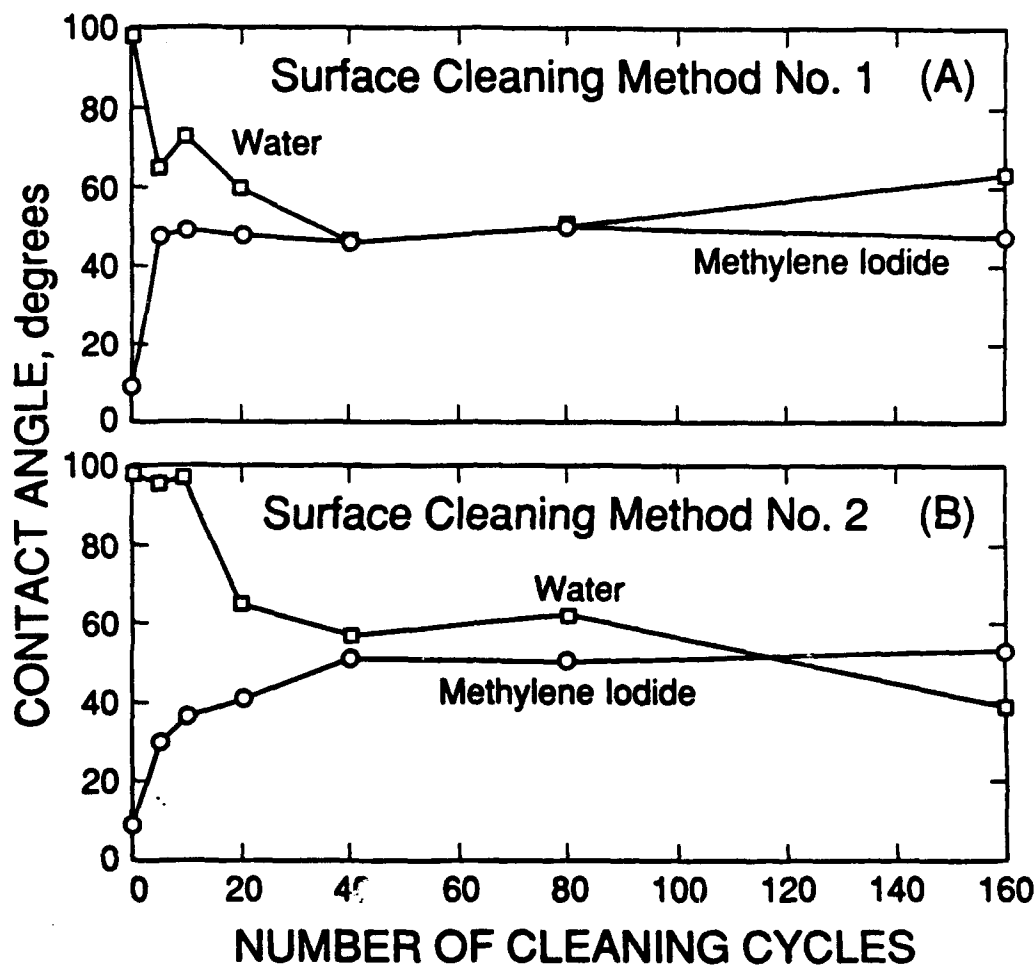


Figure 7. Contact Angles for Water and Methylene Iodide as a Function of Number of Cleaning Cycles.

components of inorganic oxides are much higher than those of hydrocarbons. For example, the nonpolar components of SiO_2 and Al_2O_3 are 78 and 100 mJ/m^2 , respectively.²¹ Based on a comparison with these data from the literature, the contaminants on the uncleaned, aged EPDM were apparently inorganic materials. However, because the measured nonpolar component of the surface of the uncleaned, aged EPDM was lower than that of inorganic oxides, some nonpolar sites on this surface were probably covered by organic materials.

As the aged EPDM rubber was cleaned with a nonpolar solvent (method No. 1), the polar component of the surface free energy and polarity increased (Table 5). This was observed even after only five cleaning cycles. This increase in polar component and polarity indicate that some of the nonpolar and low-polarity materials on the surface of the uncleaned, aged rubber were removed and that polar sites were exposed. Since 5 cleaning cycles left the rubber substantially covered with particles (Figure 3), it was assumed that the increase in polarity was due, in part, to exposure of polar sites of the inorganic

²¹ A.J. Kinloch.

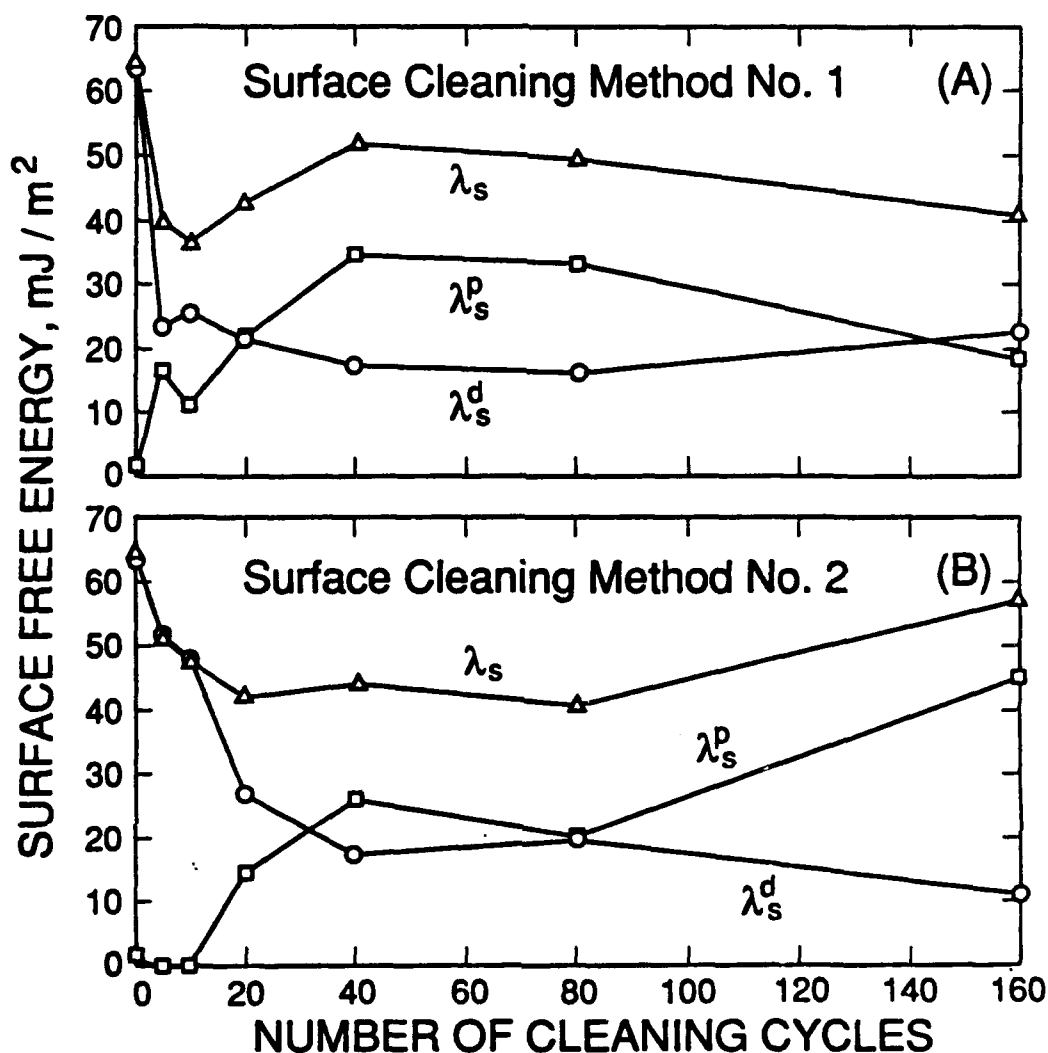


Figure 8. Surface Free Energies of Aged EPDM as a Function of Number of Cleaning Cycles.

contaminant. The increase of the polar component and the polarity as the number of cleaning cycles increased (up to 40 cycles) indicates that the nonpolar and low-polarity organic materials were further removed by the repeated cleaning.

The low contact angle (high wettability) value of water after 160 cycles using method No. 2 may have been due to residual water on the surface of the specimen at the time of the measurement. This sample, which was considered to be reasonably well cleaned, displayed a higher value of the polar component as compared to that of the well cleaned (method No. 16), aged rubber. Consistent with this supposition of water on the surface, FTIR results for specimens cleaned with the 75/25 heptane/MEK solution presented later in this chapter indicate the presence of water molecules. Consequently, the contact angle data for 160 cleaning cycles with method No. 2 were not considered representative of the cleaned surface.

Contact Angle Results for Various Cleaning Methods

Specimens used for contact angle measurements as a function of the different surface cleaning methods were taken from the same cleaned, aged EPDM samples that were used for peel strength measurements. Four contact angles were obtained on two duplicate specimens (from Set 1 and Set 2) for each surface cleaning method. Thus, eight contact angle measurements were obtained for each liquid (i.e., water and methylene iodide) and each cleaning method.

Figure 9 presents the results of the contact angles of water and methylene iodide on the aged EPDM rubber after cleaning by the 16 different methods. The contact angles shown are the individual values from the Set 1 and Set 2 samples, and indicate the reproducibility of the measurement within and between the sets.* Within any of the sets, the coefficients of variation were 15 and 10 percent or less for water and methylene iodide, respectively. More variability was observed between sets for water than for methylene iodide. For most of the cleaning methods, the two data sets for water contact angles were statistically different (0.03 level or less). Only for methods No. 1, 5, and 14 were no differences between sets found. In contrast, for the methylene iodide contact angles, no statistical differences (0.07 level or greater) were observed, except for cleaning methods No. 1, 7, and 10. Overall analysis of the data indicate that there were no significant differences between the two sections of rubber from which Set 1 and Set 2 were cut. In analyzing the data shown in Figure 9, no relationships between contact angle and cleaning method were found.

Table 6 summarizes the contact angle results and wettability parameters for the different surface cleaning methods. For each cleaning method, the listed values are the averages of all eight specimens.

As given in Table 6, all cleaning methods produced aged EPDM rubber surfaces having average contact angles for methylene iodide ranging between 44-56 degrees. This suggested that regardless of the cleaning method, the interactions of the cleaned surfaces, with an essentially nonpolar liquid were generally comparable. This result has practical significance because it implies that a number of cleaning methods would provide surfaces that would have similar wettability characteristics to nonpolar solvent-based adhesives.

The lowest methylene iodide contact angle (44 degrees) was from cleaning with tap water without a detergent (method No. 5). This result suggests that this cleaning method left more nonpolar or low-polarity organic contaminants on the surface than did the other methods. The relatively high value of the nonpolar component supports this interpretation of the data.

The average contact angles for water varied more widely than did those for methylene iodide, ranging from 45 to 84 degrees (Table 6). In the case of water, the lower contact angles indicate surfaces of greater polarity. Except for the experimental silane treatments (No. 12-15), the lowest contact angles were obtained with specimens cleaned by methods No. 1, 6, and 10. This suggests that these methods were relatively effective in removing nonpolar contaminants. In support of this interpretation, the polar components were also relatively high, indicating highly polar surfaces. The polar nature of the surfaces may have been due either to removing a substantial amount of nonpolar organic contaminants from the aged EPDM (method No. 1) or to the presence of residual water on the surface (methods No. 6, 8, and 10). As will be discussed in the following section, the FTIR results indicate that specimens cleaned with water and other polar solvents left residual water on the surface. Differences in the contact angle data among the four experimental cleaning methods (No. 12-15) were observed. However, since the peel test results for the specimens cleaned by these four methods indicate that they did not enhance adhesion,

* Some data points are not seen for some sets because they were identical or very close to other values.

Table 6

Contact Angles and Wettability Parameters for the Surface Cleaning Methods

Cleaning Method No.	CH ₂ I ₂	Contact Angle ^a degrees		Surface Free Energy mJ/m ²		Polarity γ_s/γ_t
		H ₂ O	γ_s	γ_s	γ_t	
1	52	48	14.5	36.3	50.8	0.71
2	51	65	20.8	18.8	39.6	0.46
3	47	62	22.3	19.2	41.5	0.46
4	51	68	22.0	17.5	39.5	0.41
5	44	65	25.5	15.8	41.3	0.38
6	56	50	13.5	35.7	49.2	0.72
7	48	70	25.1	12.7	37.8	0.34
8	54	51	14.9	33.3	48.2	0.69
9	50	65	21.7	17.9	39.6	0.45
10	56	45	12.3	40.6	52.9	0.77
11	54	57	16.6	27.7	44.3	0.62
12	46	47	17.8	34.1	51.9	0.65
13	47	84	33.0	3.4	36.4	0.09
14	47	81	31.0	5.2	36.2	0.14
15	47	51	18.3	30.7	48.9	0.62
16	51	71	23.5	12.9	36.4	0.35

^aAverage of eight measurements; CH₂I₂ and H₂O indicate methylene iodide and water, respectively.

further investigation of their effects on aged EPDM surfaces was not conducted. Consequently, an explanation of the differences in the contact angle data for these methods is not offered.

FTIR Spectroscopy Observations and Results

Before conducting FTIR analyses on the cleaned EPDM rubber specimens, the chemical nature of the contaminants and the contaminant-free, aged EPDM surface were investigated. Figure 10a presents the FTIR transmission spectrum of the removed contaminants. The spectrum showed the bands between 2800-3000 cm⁻¹, due to CH stretching of hydrocarbons. This finding indicates that the contaminants included organic materials, an interpretation consistent with the wettability data. The broad bands between 3200 and 3500 cm⁻¹ are normally due to the OH (and NH) stretching, which indicates that the contaminants probably contained polar materials having hydroxyl groups. The presence of these bands supported the wettability data that showed the high polar component and high polarity after removing the nonpolar organic contaminants from the surface of the aged EPDM rubber. The sharp band near 3625 cm⁻¹ in Figure 10a is probably due to isolated, adsorbed water molecules on the inorganic contaminants; bands associated with hydrogen-bonded adsorbed water molecules occur in the 3200-3500 cm⁻¹ region. Finally, the broad bands near 1000 cm⁻¹ are normally characteristic of silicates and phosphate inorganic materials.

Figure 10b is the FTIR-ATR spectrum of aged EPDM rubber cleaned by method No. 11. The surface of this specimen was essentially free of platelet particles and the rubber being quite visible, as shown from its SEM image (in the following section). Figure 10b shows strong absorption bands in the 2800-3000 and 850-1050 cm⁻¹ regions. Again, the bands in the 2800-3000 cm⁻¹ region are due to the CH stretching. The band peaking at 970 cm⁻¹ may be due to the CH out-of-plane deformation of the

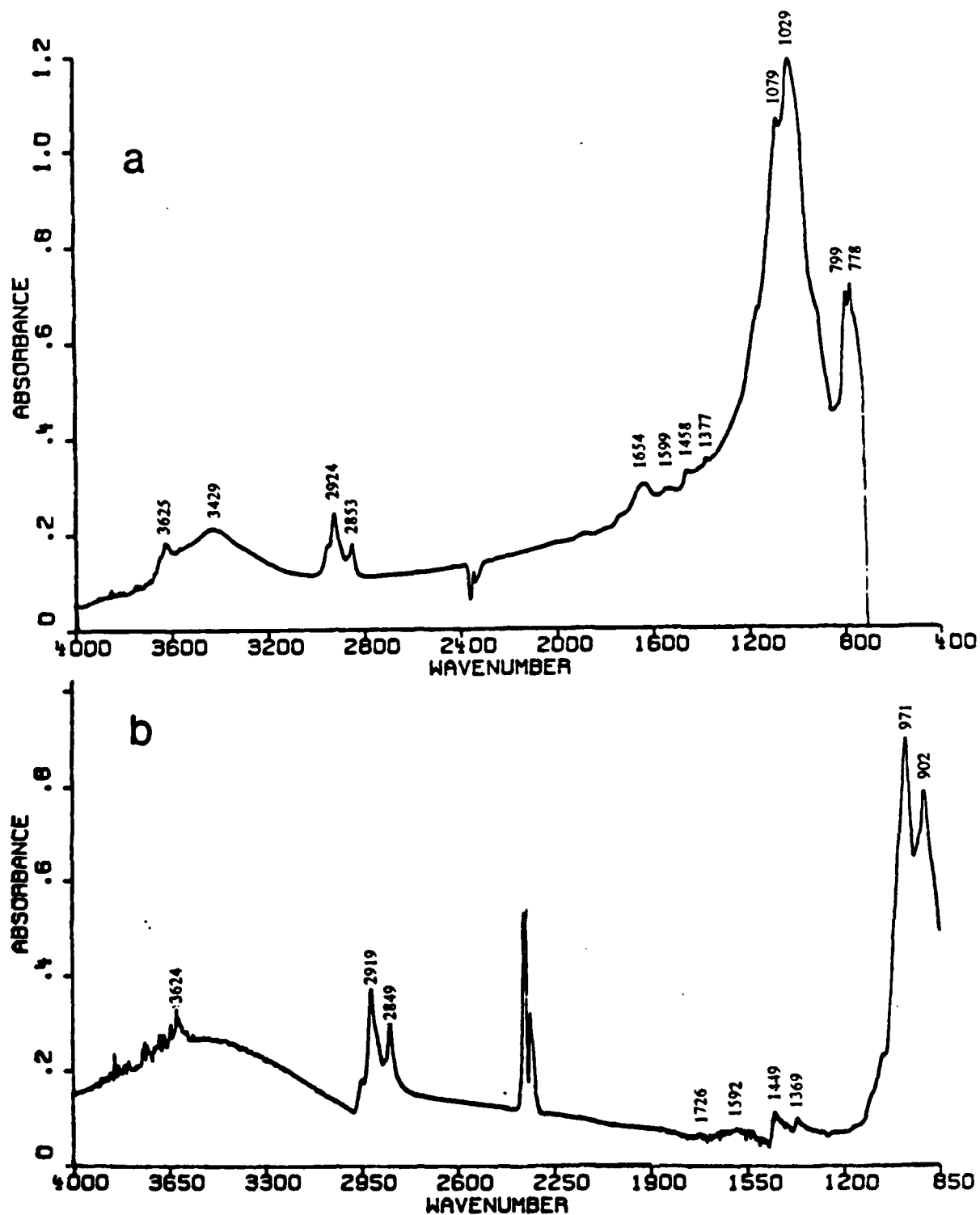


Figure 10. Example of FTIR Spectra for (a) Contaminants Removed From Surface and (b) Cleaned Surface of EPDM.

vinylidene group of the unsaturated monomer used for cross-linking. For example, the CH deformation of the vinylidene group in 1,4-hexadiene occurs at 966 cm^{-1} .²² The strong band at 904 cm^{-1} was not assigned at this time. The band near 3625 cm^{-1} suggests that water was present on this cleaned surface. The broad band in the $3100\text{--}3600\text{ cm}^{-1}$ region and the very weak band occurring near 1725 cm^{-1} indicates the presence of OH and C=O groups, respectively. Careful examination of FTIR spectra of cleaned, new EPDM rubbers (not shown) did not detect these bands. Thus, their presence in the aged rubber suggests possible oxidation of the material's surface with time. Further study is needed to provide conclusive evidence, however.

FTIR-ATR spectra were obtained on specimens of the aged EPDM rubber cleaned by methods No. 1-10. Lines a, b, c, and d in Figure 11 present representative spectra and compare specimens that were: uncleaned, cleaned with heptane (method No. 1), cleaned with a proprietary wash solution (method No. 4), and cleaned with tap water, respectively. In general, there were only minor differences in the spectral characteristics of the cleaned aged specimens, as illustrated in Figure 11. The spectral characteristics of the cleaned specimens included the bands in the $2800\text{--}3000\text{ cm}^{-1}$ region and the bands peaking at 970 and 904 cm^{-1} . These bands were assigned as previously discussed for cleaned, aged EPDM.

In comparison to the spectra of the cleaned specimens, the spectrum of the uncleaned, aged EPDM (Figure 10) also showed bands peaking at 983 and 914 cm^{-1} . Because these bands were not present in the spectra of the cleaned specimens, they probably resulted from contaminants on the uncleaned EPDM. Note, however, the closeness of these bands of the contaminants and bands at 970 and 904 cm^{-1} of the cleaned, aged EPDM rubbers. This closeness complicates interpretation of the spectra of the cleaned specimens. For example, it was shown using SEM analysis (see following section) that many surfaces of the cleaned specimens contained platelet particles typical of a release agent. Because release agents are silicate materials (talc or mica), they would be expected to produce a band in the region of 1000 cm^{-1} . However, this band overlaps the higher-frequency end of the 970 cm^{-1} band associated with the EPDM. Consequently, FTIR analysis could not resolve whether the surfaces of the cleaned rubber specimens had a talc-like release agent on them.

The spectra of the specimens cleaned by methods No. 2-10 contain a band near 3625 cm^{-1} . This band was due to molecular water, as previously stated. Its presence was attributed to cleaning with methods that included polar solvents or water. The band was not present in the spectrum of the surface cleaned with heptane (method No. 1).

The specimen cleaned with method No. 4 produced a spectrum with several additional bands in the $1200\text{--}1500\text{ cm}^{-1}$ region. In this case, the band shapes in the $2800\text{--}3000\text{ cm}^{-1}$ were also different. The additional bands may be due to the coating deposited on the surface of the aged EPDM rubber when cleaned using method No. 4 (see next section).

In summary, FTIR-ATR spectroscopy is useful for distinguishing cleaned, aged EPDM from uncleaned, aged EPDM. It may also provide valuable information on whether a cleaning method has modified the surface, such as leaving behind a polymeric coating or residual water. No major differences were observed among the FTIR spectra of any of the cleaned specimens that were tested.

²² K. Fujimoto, and K. Wataya, "The Study of Polymers by High-Temperature ATR Spectroscopy," *Journal of Applied Polymer Science*, Vol 13 (1969), pp 2513-2526.

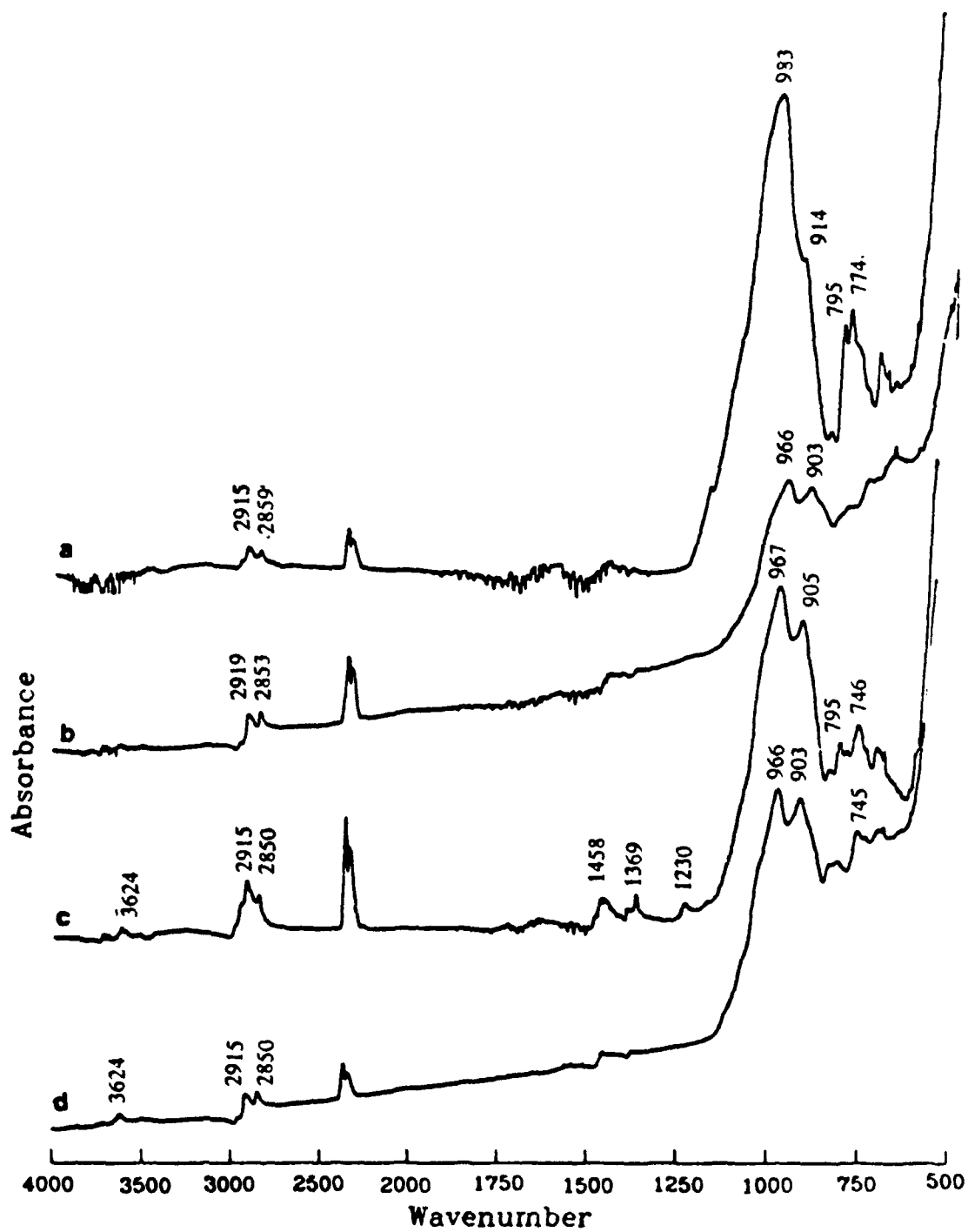


Figure 11. FTIR-ATR Spectra of Aged EPDM Cleaned by Four Different Methods.

Scanning Electron Microscopy Observations and Results

A section of each aged EPDM specimen cleaned by methods No. 1-12 and No. 16 were subjected to SEM surface analysis. (Specimens cleaned by methods No. 13, 14, and 15 were not subjected to SEM analysis since part of those methods involved modification of the surface with a tackifier, as discussed previously.) The SEM observations, based on visual examination of the photomicrographs, are summarized in Table 7.

The most notable feature was the presence of platelet particles indicating release agent on the surfaces of most of the specimens (methods No. 1-3 and 5-10). Figure 12a presents a typical photomicrograph showing the surface of a specimen covered with the platelet particles. In the cases where platelet particles were visible, it was not possible by visual examination of the micrographs to tell whether the amount varied between specimens as a function of the cleaning method. Qualitatively, all micrographs of surfaces with platelets appeared to be comparable regardless of the cleaning method employed.

The presence of platelet particles on the surfaces of these specimens was not surprising in that the original rubber sheet had been coated with a release agent during its manufacture. In service, the release agent was not washed free by rain or other means. It stayed in place and became covered with the layer of dirt noted previously. The SEM observations indicated that the specimens were not totally cleaned under methods No. 1-3 or 5-10. In the present study, most of the cleaning methods apparently removed the relatively loose particles from the surface while leaving behind those that were more strongly bonded to, or perhaps partially embedded in, the rubber surface. As a consequence, the peel specimens cleaned by methods No. 1-3 and 5-10 contained release agent at the interface of the tape and the rubber surface.

Only in the case of cleaning methods No. 11 and 16 were the rubber surfaces observed to be essentially free of platelet particles (Figure 12b). In contrast to the methods where particles remained on the surface after cleaning, these methods No. 11 and 16 involved relatively vigorous mechanical abrasion: the former used a wire brush attached to an electric drill and the latter employed extensive hand scrubbing with a stiff bristle brush (Table 3). Nevertheless, although the rubber surfaces were cleaned essentially free of release agent, the peel strength of the bonds formed with the tape were not significantly greater than those made on rubber which still contained release agent after washing with heptane (Table 4).

Table 7

Summary of the SEM Observations of Cleaned EPDM Specimens

Cleaning Method No.	SEM Observations
1 - 3, 5 - 10	Surface substantially covered with platelet particles indicative of release agent.
4	Surface was smooth and appeared to be coated or covered with a residue; platelet particles covered with the residue could be observed.
11 & 16	The rubber surface was plainly visible and essentially free of platelet particles.
12	Surface appeared to be coated or covered with a residue; in some locations, platelet particles covered with residue could be observed.

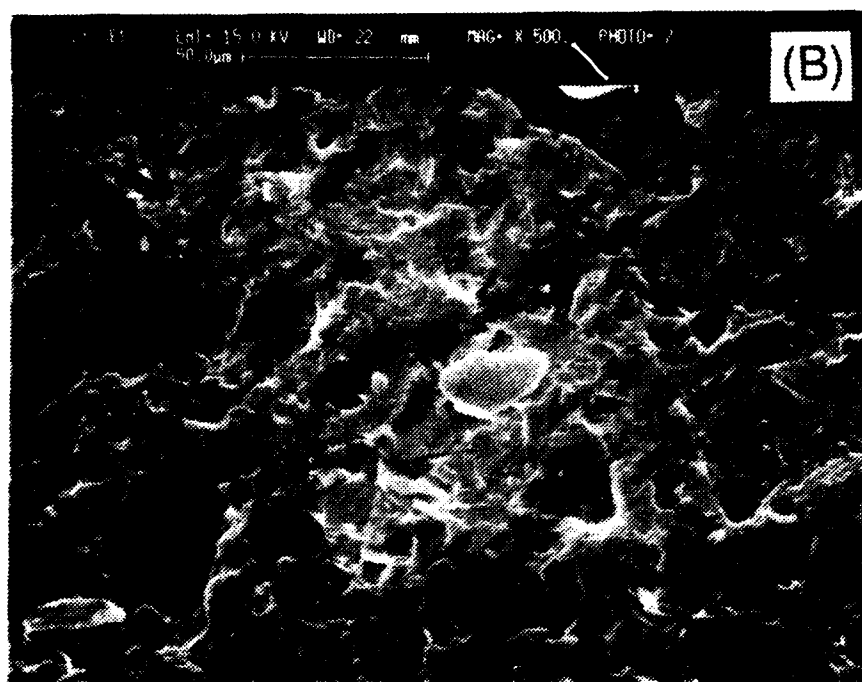
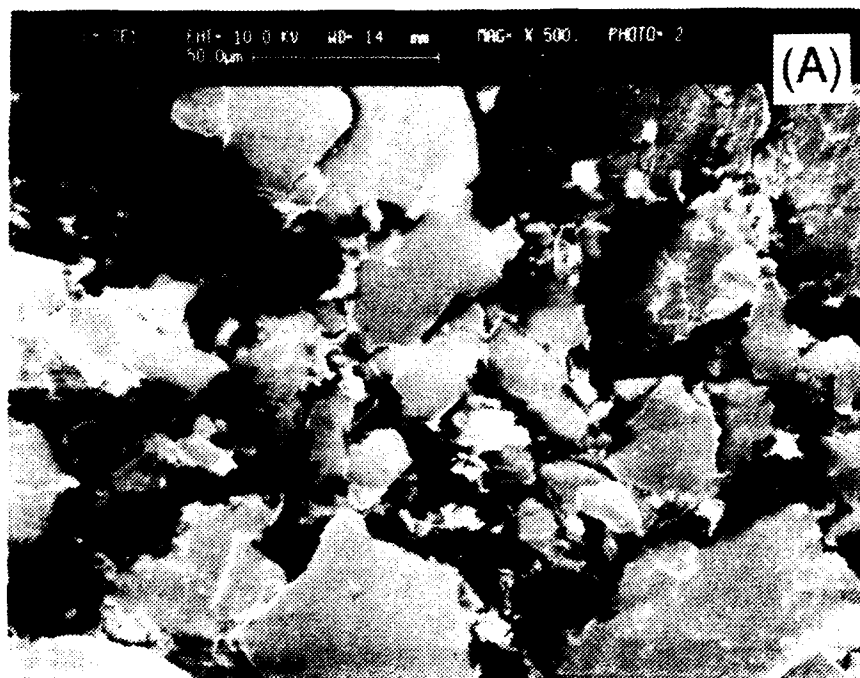


Figure 12. SEM Photomicrographs of EPDM Specimens.

For the specimens that had been cleaned using methods No. 4 and 12, SEM analyses indicated that a coating, which generally covered the release agent particles, had been deposited on the specimen surfaces (Table 7). The tape used to form the peel specimens was adhered to this coating. For cleaning method No. 4, the coating apparently had a positive effect in that the average peel strength of these specimens was the highest of any measured for any of the cleaning methods (Table 4). In contrast, the average peel strength of the specimens cleaned under method No. 12 was among the lowest measured for the specimen sets.

Creep-Rupture Experiment

It has been reported that creep-rupture tests of joint specimens in a peel configuration offer a sensitive method for assessing factors affecting the performance of seams.²³ In a creep-rupture experiment, a joint specimen is placed under load, and the time over which it sustains the load before total delamination is measured. This time period is called the "time to failure" for the specimen.

In the present study, joint specimens (Appendix B, Figure B2) prepared from one strip of cleaned, aged rubber (method No. 1) and a strip of cleaned, new rubber (method No. 16) were subjected to creep-rupture testing. This set of laboratory specimens was considered comparable to field patches (i.e., new rubber bonded to aged rubber), and was designated CR1. Heptane was selected to clean the aged rubber because it produced a relatively high peel strength in the comparative cleaning experiments (Table 4) and was similar to the method most commonly used in the field to clean aged EPDM before patching or splicing. As a control for the creep-rupture experiment, joint specimens were also prepared using two new strips of rubber cleaned by (method No. 16). This set of specimens was considered comparable to new field seams (i.e., new rubber bonded to new rubber), and was designated CR2.

Before conducting the creep-rupture tests, the short-term peel strengths of five replicate joint specimens from each set (CR1 and CR2) were determined. The two sets of specimens performed comparably in the tests. The average strengths of the CR1 and CR2 sets were 0.77 and 0.82 kN/m (4.4 and 4.7 lbf/in.), respectively (Table 8), and were not significantly different (0.05 level). The locus of failure of all five CR1 specimens was at the interface of the tape and the new rubber. These results indicate that cleaning aged EPDM rubber by wiping the surface with a cloth soaked with heptane produced bonds with the tape that were, under the peel-test conditions, stronger than those obtained with new, cleaned rubber and the tape.

For each of the two sets (CR1 and CR2), 14 joint specimens were subjected to creep-rupture testing under a load of 4.2 N (0.94 lbf). This was approximately 20 percent of the average short-term strength of the specimens (Table 8). The results of the creep-rupture tests are given in Figure 13, wherein it is evident that the two specimen sets performed differently under the creep conditions. As just described, this finding was in contrast to that for the short-term strength tests, where the CR1 and CR2 specimens performed comparably. Consistent with the short-term peel strength tests, the CR1 specimens failed at the interface of the new cleaned rubber with the tape. Cleaning the surface of the aged EPDM rubber by wiping with a cloth soaked with heptane provided a bond with the tape that was more resistant to peel under creep conditions than that of the new cleaned rubber.

Martin et al.²⁴ have shown that creep-rupture times to failure of EPDM joint specimens fabricated with solvent-based adhesives fit a Weibull distribution that has the form:

$$F(t) = 1 - \exp(-t/\beta)^\alpha) \text{ for } t > 0 \quad [\text{Eq 1}]$$

²³ Jonathan W. Martin et al., May 1990.

²⁴ Jonathan W. Martin et al., May 1990; Jonathan W. Martin et al., April 1987.

Table 8
Summary of Results for Creep-Rupture Experiment

Test No.	Short-term Peel Tests			Creep-rupture Tests			
	range	av	COV ^a	load	load	time-to-failure	
	lb/in.	lb/in.		lb	ratio ^b	mean	s.d. ^c
	(kN/m)	(kN/m)	%	(N)	%	min	min
CR1	4.2 - 4.6 (0.74 - 0.81)	4.4 (0.77)	4	0.94 (4.2)	21	247	29
CR2	4.4 - 5.1 (0.77 - 0.89)	4.7 (0.82)	7	0.94 (4.2)	20	420	99

^a Coefficient of variation.

^b Ratio of the load applied under creep-rupture conditions to the average short-term peel strength.

^c Standard deviation.

where: $F(t)$ is the Weibull distribution function and 100 times $F(t)$ equals the cumulative percent failed
 $\alpha > 0$ and is the Weibull shape parameter
 $\beta > 0$ and is the Weibull scale parameter
 t is time.

Statistical analysis of the CR1 and CR2 creep-rupture data in the present study showed that each data set displayed a good fit to the Weibull distribution function. Moreover, the analysis verified the distinctive nature of the two data sets evident in Figure 13. For the CR1 data set, the values of the α and β parameters were 9.8 and 260, respectively. For the CR2 data set, the values were 5.3 and 454, respectively. For the two data sets, the differences between the α and β parameters were statistically significant.

Reasons why the data for the CR1 and CR2 specimen sets were different in the creep-rupture tests, while being indistinguishable for the short-term strength tests, were not investigated in this study. It may be that subtle differences in the mechanics of peel testing due to factors such as the stiffness or thickness of the EPDM strips comprising the joint specimens were amplified under creep testing in the peel configuration. Such factors can influence adhesion tests.²⁵ Note in Table 1 the difference in thickness and modulus values between the new and aged rubbers.

Although an explanation of these results is not given here, the observation illustrates the proposition that creep-rupture testing is a more sensitive method than short-term strength tests for assessing factors affecting seam performance.²⁶ Although all specimens in both the CR1 and CR2 sets failed at the

²⁵ Souheng Wu, 1987; A.J. Kimloch, 1987.

²⁶ Jonathan W. Martin et al., May 1990.

interface of the tape and the new EPDM rubber, some factor caused the CR2 specimens to have significantly longer times-to-failure than the CR1 specimens. An understanding of this observation might provide further insight into means for extending seam creep-rupture life.

SEM analysis was conducted on the cleaned surfaces of both the aged and new rubbers used in the creep-rupture experiments. The results were similar to those obtained from the SEM analyses of the rubber samples subjected to the various cleaning methods (Table 4). In the creep-rupture experiment, the aged rubber cleaned by method No. 1 was found to have platelet particles on its surface. In contrast, the new rubber cleaned under method No. 16 was seen to have a surface essentially free of release agent. These observations indicate that, under the conditions of both the short-term strength and creep-rupture tests, the interface between the platelet-free surface of the new rubber and the tape was more prone to failure than that between the surface of the aged rubber with release agent and the tape. Reasons for this were not explored in this study.

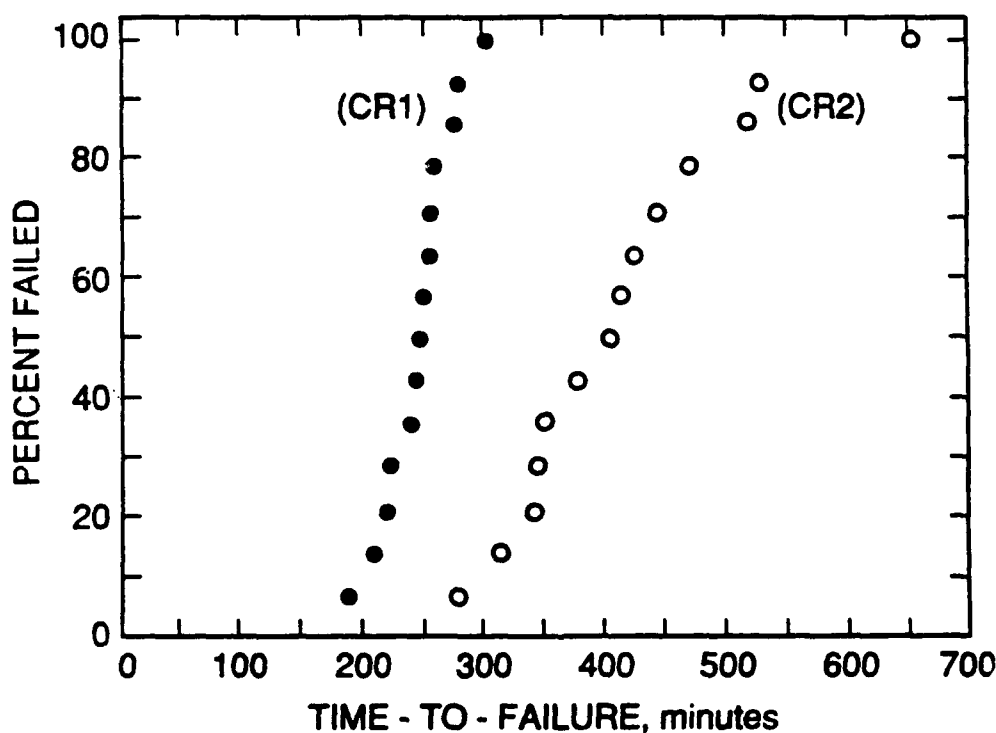


Figure 13. Graph of Creep-Rupture Experiment Results.

4 COMPARISON OF THE RESULTS OF THE DIFFERENT TEST METHODS

Although peel tests of bond strength are a routine exercise for laboratory evaluation, they are two time consuming, and more importantly, destructive to be highly practical in the field. On the other hand, surface characterization by some other techniques may provide important information for assessing the surface condition of aged EPDM rubber before bonding a patch to it. For this reason, the peel strength data for the cleaned, aged rubber specimens were compared with the information obtained by the surface analytical techniques—particularly contact angle—to look for evidence of systematic relationships. Table 9 summarizes the results of the peel strengths and surface analyses of the specimens cleaned by the various methods.

Comparison of Peel Strength with SEM and FTIR Findings

From a comparison of the peel strengths with the SEM results, it was concluded that the SEM technique was not able to distinguish a surface that produced a seam with relatively high peel strength from a surface that gave rise to a seam with low peel strength. Similarly, in comparing the peel strengths with the FTIR spectra, it was found that the FTIR-ATR technique could not differentiate between surfaces providing bonds of different strength.

Comparison of Peel Strength to Contact Angle Findings

An attempt was made to relate the peel strengths to the contact angle data for the 16 surface cleaning methods. Reports of good relationships between bond strength and contact angle parameters for homogeneous substrates have previously been published,²⁷ but in the present study, no evidence of such relationships was observed between any of the contact angles (or wettability parameters) and peel strength. One reason for this apparent inconsistency may be that local chemical and topographical differences in the surfaces prepared by the different cleaning methods provide inhomogeneous substrates and, thus, have a substantial effect on the contact angle measurements. In contrast, the bond strength measurements, which averaged out the entire surface area, are probably more forgiving of local differences in surface condition. Another reason for the apparent inconsistency is that the wettability parameters are derived from the theoretical and ideal interaction between a liquid and a solid,²⁸ whereas the peel strength between a substrate and a solid adhesive tape depends not only on the interaction of the two solid bodies but also on interfacial defects and other specific conditions affecting the quality of seam formation.

Relationship of Peel Strength, Contact Angle, and Cleaning Cycles

When peel strength and contact angle of water were plotted as a function of the number of cleaning cycles, the relationship in Figure 14 was found. In this figure, with one exception, all strength and contact angle data points for each cleaning-cycle number were the average values obtained from both cleaning methods No. 1 and 2. In the case of the contact angle value at 160 cycles, only data from cleaning method No. 1 were used. As discussed in the Chapter 3 subsection "Effects of Cleaning Cycle on Contact Angle Measurements," the contact angle measurement of water after cleaning with method No. 2 for 160 cycles appeared to be unduly influenced by the presence of water molecules on the surface and, therefore, it was not considered truly representative of the cleaned surface.

²⁷ Souheng Wu, *Polymer Interface and Adhesion*, Section 14.7 (Marcel Dekker, New York, 1982).

²⁸ A.N. Gent and G.G. Hamed.

Table 9

Summary of Peel Strength, Contact Angle, FTIR, and SEM Results for the Various Cleaning Methods

Cleaning Method No.	Peel Strength		Contact Angle ^a		FTIR ^b Spectroscopy	SEM ^c Observations
	Average		degrees			
	lbf/in.	kN/m	CH ₂ I ₂	H ₂ O		
1	7.1	1.2	52	48	no water	platelets
2	7.9	1.4	51	65	water	platelets
3	5.6	1.0	47	62	water	platelets
4	9.8	1.7	51	68	water	coated
5	6.2	1.1	44	65	water	platelets
6	6.3	1.1	56	50	water	platelets
7	5.9	1.0	48	70	water	platelets
8	4.6	0.8	54	51	water	platelets
9	6.0	1.1	50	65	water	platelets
10	5.4	0.9	56	45	water	platelets
11	7.2	1.3	54	57	water	plate. free
12	5.3	0.9	46	47	not run	coated
13	5.0	0.9	47	84	not run	not run
14	5.1	0.9	47	81	not run	not run
15	5.3	0.9	47	51	not run	not run
16	6.3	1.1	51	71	not run	plate. free

^aCH₂I₂ and H₂O indicate methylene iodide and water, respectively.

^bWith the exception of the presence of residual water (as indicated below), no major differences between the FTIR spectra of the specimens cleaned using the various methods were observed.

^cThe major observations from the SEM analyses were; (1) a surface covered with platelet particles indicative of release agent, (2) a coated surface, and (3) a surface free of release agent.

Figure 14 shows that as the number of cleaning cycles was increased from 0 to 40, the water contact angle decreased and the peel strength increased. With further cycling, both the contact angle and the peel strength increased.

Figure 14 provides an explanation of the increase in peel strength as a function of the number of cleaning cycles from a surface-analytical point of view. During the initial cycling (0 to 40 cycles), the more nonpolar and low-polarity contaminants were removed from the surface of the rubber, exposing a more polar surface with lower water contact angles. This change in polarity, together with a continuing reduction of loose particles on the rubber surface, produced a relatively rapid increase in the peel strengths of the seam specimens. Subsequently, after most of the loose particles were removed (greater than 40 cycles), further cycling gave the surface more nonpolar characteristics, which consequently produced a slight increase in the water contact angle. This increase in the water contact angle was attributed to greater exposure of the less polar surface area of the EPDM rubber. The increase in contact angle was accompanied by an increase in the peel strength, but at a relatively lower rate.

A Possible Surface Condition Test Based on Wettability Parameters

The data in Figure 14 suggest that the contact angle of water might be useful in the field to assess the bonding condition of the EPDM surface after cleaning. Based on these data, after removal of the substantial amount of loose surface particles and other contaminants, the water contact angle on the

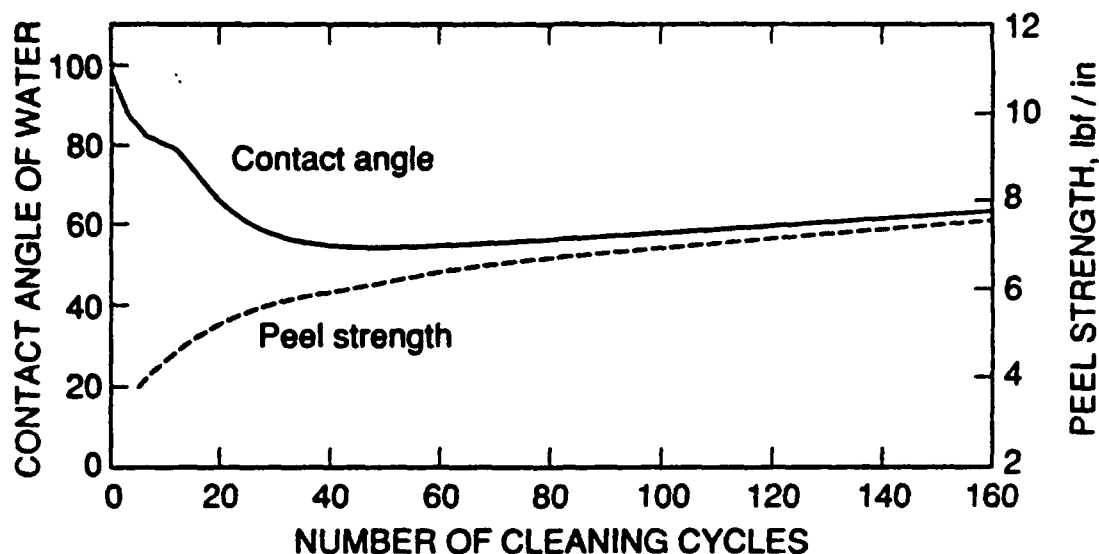


Figure 14. Relationship Between Peel Strength and Water Contact Angle as a Function of Cleaning Cycles.

cleaned rubber should be greater than 55 degrees. However, the direct use of such a criterion is not practical because there is no simple method for estimating the contact angle of a liquid on EPDM rubber in the field.

It was known from the initial data obtained in the preliminary phase of the present study²⁹ that the spreading coefficient of water increased as the level of contamination on new EPDM increased. In other words, if the surface was not well cleaned, the water contact angle would decrease more rapidly with time as compared with that for a well cleaned surface. The decrease in contact angle with time would be observed as the spreading of a drop of water placed on the rubber. If the spreading coefficient of water could be used as a criterion of cleanness, there would be no need to measure the contact angle. Instead, the rate of spreading (or the change in size of the droplet) on the rubber surface as a function of time could be estimated, and allowable limits for a given period of time could be prescribed.

Preliminary tests of the spreading tendency of water on the surface of the specimens cleaned in this study showed that water was not a suitable liquid. Specifically, using the size of the drop as an indicator, it was not possible to observe differences in the spreading of water for the various cleaned specimens as a function of the number of cleaning cycles. Consequently, other liquids were investigated.

Dimethyl formamide (DMF) was found to be sensitive to differences in surface condition achieved with the various cycles of cleaning. In particular, when the rubber was reasonably well cleaned (80 and 160 cycles), the size of a 7-8 mm drop of DMF essentially went unchanged after 5 minutes or more. When the number of cycles was 20 and 40, the drop spread to greater than 10 mm in about 5 minutes or less. Finally for the uncleaned and slightly cleaned surfaces (5 and 10 cycles), the drop spread spontaneously upon being placed on the surface. In addition, drops of DMF placed on the surfaces of the specimens cleaned for 80 cycles according to the various cleaning methods (Table 3) did not spread appreciably within 5 minutes. These results were confirmed qualitatively, remaining consistent for repeated tests.

²⁹ Walter J. Rossiter, Jr., et al., February 1991.

Based on these limited data, as a preliminary step toward developing a simple surface condition test for cleaned EPDM, it is suggested that a "droplet test," using a spreading drop of DMF as described above, be used in the field on an experimental basis. This would provide a means for obtaining field data on this proposed test, which has not yet been investigated in the field.

5 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Summary

This study investigated the relative effectiveness of different cleaning methods used for preparing the surface of aged EPDM roofing membrane material for patching. The effectiveness of the cleaning methods was evaluated using tests of short-term strength and long-term creep rupture in peel. The membrane materials were also analyzed through scanning electron microscopy, Fourier transform infrared-attenuated total reflection spectroscopy, and contact angle measurements for liquids resting on EPDM surfaces. A section of an aged ballasted EPDM membrane, cut from a roof after 10 years in service, was used in the study. The surface of the rubber was cleaned using a mechanical abrasion device that repeatedly rubbed a brush or cloth in a reproducible manner across the surface of the EPDM sample. Water-based and solvent-based cleaning solutions were used, most of which were based on procedures typically used in the field to prepare the surface of aged EPDM rubber for patching.

Key findings of this study include the following:

- The uncleaned, aged EPDM rubber surface was covered with contaminants whose outermost layer was nonpolar. The uncleaned rubber would not form a bond to an adhesive tape that is used in practice to fabricate EPDM seams. After removal of some contaminants, joints with relatively low peel strength could be formed with the tape.
- As the number of cleaning cycles increased using nonpolar and low-polarity solvents, the peel strength of the joints increased. The water contact angle decreased (i.e., the nonpolar surface free energy component increased) with the first few cycles. After most of the contaminants were removed by more cleaning cycles, the contact angle for water slightly increased. This was attributed to an increase in the amount of exposed surface area of the less polar rubber.
- All cleaning methods provided aged EPDM rubber surfaces that formed joints with the tape whose peel strengths were comparable to bonds formed between solvent-based adhesives and new EPDM rubber. Statistically significant strength differences were found between some of the cleaning methods. Joints prepared by wiping with heptane, a method similar to the common field procedure of washing with unleaded gasoline, gave peel strengths that were among the highest measured. The strength of these joints was statistically higher than for joints prepared by cleaning the aged rubber with water-based methods. Short-term strength and creep-rupture joints, prepared by tape-bonding the surface of the heptane-cleaned aged EPDM to a surface of well cleaned, new EPDM, failed in peel at the interface between the tape and the new rubber.
- No relationships between contact angle and cleaning method were found. In particular, the methylene iodide contact angle varied only slightly as a function of cleaning method. This result implied that a number of cleaning methods would provide surfaces with similar wettability characteristics for nonpolar-solvent-based adhesives.
- The FTIR technique could distinguish the uncleaned, contaminated surface of the aged EPDM from those that were well cleaned or coated during cleaning. Only minor differences between the FTIR spectra of the specimens cleaned using the various methods were observed.
- SEM analysis was the only technique that distinguished particle-free surfaces from those that retained release-agent particles after cleaning. In samples where particles were still present after cleaning,

SEM analysis could not distinguish any differences related to the methods. Through SEM analysis, it was found that vigorous mechanical abrasion was the only cleaning method that provided an aged EPDM surface essentially free of release agent.

- No relationships were observed between peel strength and the SEM, FTIR, or contact angle data for the surfaces cleaned using any of the various methods. However, from a surface analytical point of view, contact angle measurements provided an explanation for the increase in peel strength as a function of cleaning cycles: the contact angle for water increased with larger numbers of cleaning cycles, which corresponded to greater exposure (i.e., contaminant removal) of the EPDM rubber's surface.

- The rate of spreading, or the change in size over time, of a liquid droplet placed on the aged EPDM rubber was suggested as a means for assessing the condition of its surface after cleaning. Water was not suitable for this purpose. Dimethyl formamide (DMF) appeared to be suitable, however, as it was sensitive to differences in surfaces having various levels of cleanliness. The rate of spreading (or change in the size) of a droplet of DMF placed on cleaned, aged EPDM rubber might form the basis of a surface-cleanliness criterion suitable for use in the field.

Conclusions and Recommendations

Based on the results of this laboratory study, it is concluded that

- Aged EPDM membrane materials may successfully be cleaned for patching
- A simple test using a droplet of DMF may accurately indicate the surface bonding condition of aged EPDM.

It is recommended that the following guidelines be observed in field cleaning and assessment of EPDM roofing membrane surfaces when repairs are to be made:

- All visible contaminants should be removed and the dark black or bright white color, typical of well cleaned new black and white EPDM sheets, respectively, should be restored. This may be accomplished with solvent wipe or detergent scrub techniques commonly used in practice. When using a solvent wipe technique, it is important to change cloths often, because they pick up contaminants from the rubber. When using a detergent scrub, it is important to rinse the brush often to remove contaminants picked up during the cleaning. When water is used in the cleaning procedure, the rubber surface should be dried (e.g., using a dry cloth) before solvent wiping.

- Vigorous mechanical abrasion (e.g., a wire brush attached to an electric drill) should be used if it is desired that the membrane surface is essentially free of release agent before making a patch.

It is recommended that the DMF droplet test be used experimentally as a preliminary step towards establishing a simple test for assessing the bonding condition of the EPDM membrane surfaces after cleaning. This experimental application would provide a means for obtaining field data on the proposed droplet test technique. The DMF should be applied using an eyedropper held vertically (i.e., about 90 degrees) about 5 mm above the rubber surface. The size to which the droplet spreads within a given period of time will indicate the wettability of the membrane to solvent-based compounds. The droplet should have an initial diameter of about 7 to 8 mm (which can be estimated using a ruler). If the surface is acceptably clean, the diameter of the droplet should not increase by more than 2 mm within 5 minutes.

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APPENDIX A: Summary of the Major Findings of the Preliminary Phase of the Study

In the preliminary phase, investigations were conducted on the use of surface analysis techniques for ascertaining whether the surface of aged EPDM rubber is properly cleaned before patches are bonded to it.³⁰ It was found that scanning electron microscopy (SEM), contact angle measurement, and Fourier transform infrared-attenuated total reflection (FTIR-ATR) spectroscopy were found to be useful for general laboratory analysis of EPDM rubber sheets. Experimental procedures were developed for this purpose for use in the main phase of the study. The major findings were as follows.

A.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy analysis was able to differentiate between the amount of release agent on the surface for three degrees of contamination (slight, medium, and heavy) with a talc-like release agent. When the sample contained only a slight deposit, the micrograph showed areas of the rubber surface visible between particles of release agent. As the amount of release agent on the rubber surface increased, the rubber surface became less visible.

A.2 Contact Angle

The preliminary results suggested that the water contact angle, the spreading rate of water on the EPDM rubber, and the polarity (or the polar component) of EPDM rubber each might provide useful indicators of surface cleanness. For EPDM rubber surfaces with varying degrees of release agent contamination, it was found that the cleaner sheets had greater contact angles and lower polarities.

A.3 Fourier Transform Infrared Spectroscopy (FTIR)

Investigations were limited to the development of a satisfactory experimental procedure for using FTIR for characterizing surface chemical compositions of EPDM membrane materials. It was found that FTIR-ATR using two reflections or less was useful for characterizing carbon black-filled EPDM roofing membrane material.

³⁰ Walter J. Rossiter, Jr., et al., February 1991.

APPENDIX B: Test Methods

Peel Tests. T-peel test specimens, measuring 150 x 25 mm (1 x 6 in.), were prepared using the cleaned rubber strips and the commercially available butyl-based tape (Figure B1). The dimensions of the bonded area delaminated in peel were 25 x 100 mm (1 x 4 in.). To prepare a test specimen, 25 x 100 mm (1 x 4 in.) and 25 x 150 mm (1 x 6 in.) pieces of butyl-based tape were adhered to the cleaned and uncleaned surfaces of an EPDM rubber strip, respectively. The release paper was left in place on the surfaces of the tape that were not adhered to the EPDM strip. The resulting rubber/tape composite was placed in a laboratory press at 1.4 MPa (200 lbf/in.²) for 5 minutes. After removal from the press, it was allowed to remain at ambient laboratory conditions (about 22°C, or 72°F, and 45-50 percent relative humidity RH) for 7 days. Then, the release paper was removed from the two exposed surfaces of the butyl tape, and replaced with strips of fiberglass packing tape. The fiberglass tape was used to prevent excessive elongation of the specimens during peel testing.

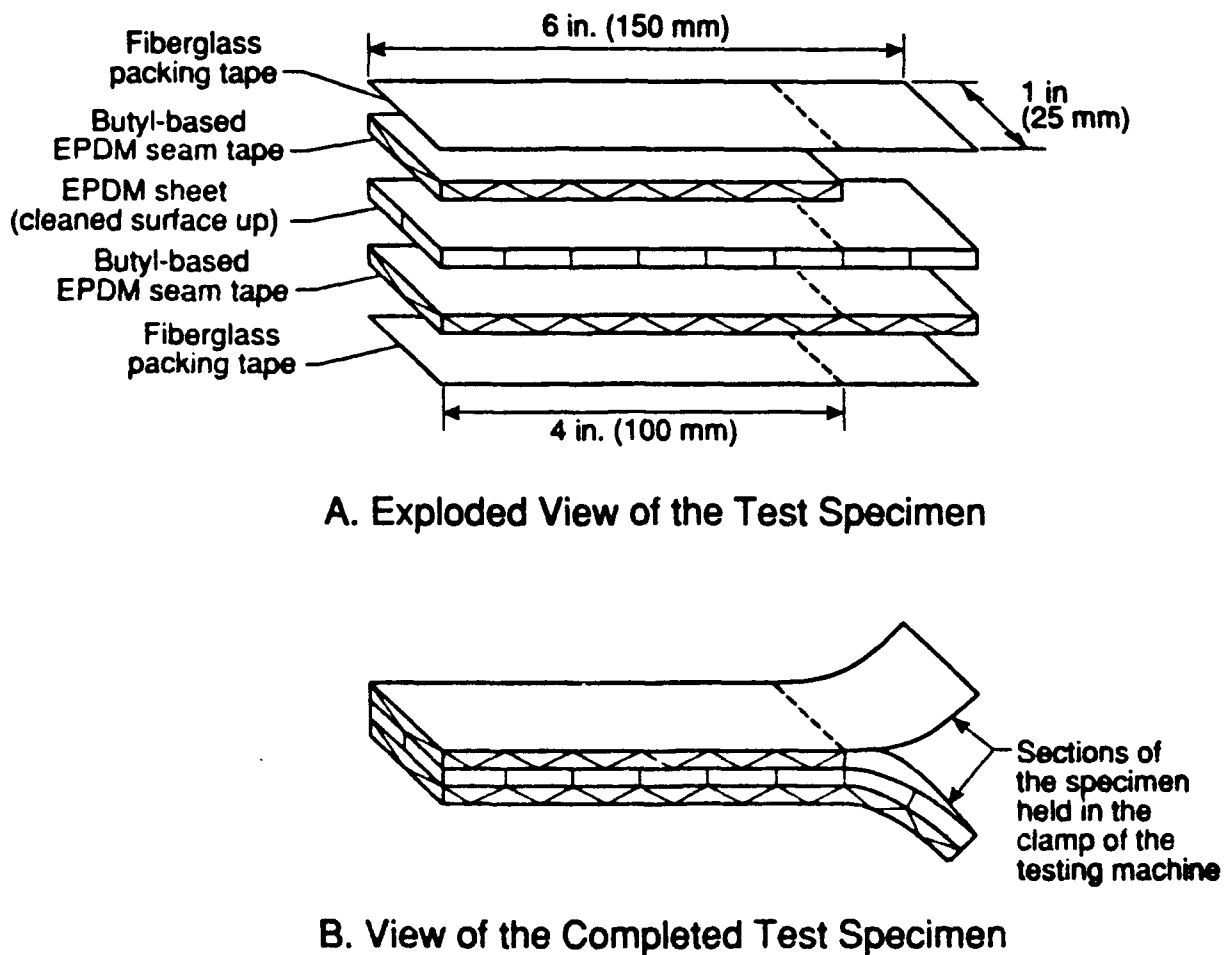


Figure B1. Configuration of the Test Specimen Used for Short-Term T-Peel Strength Measurements.

As shown in Figure B1, the specimen was clamped in a universal testing machine such that one grip held only a section of fiberglass packing tape, while the other grip clasped a section comprising the cleaned rubber strip, butyl-based tape, and fiberglass packing tape. When the specimen was subjected to peel delamination in the testing machine, the failure was interfacial between the cleaned surface of the rubber strip and the 25 x 100 mm (1 x 4 in.) piece of butyl-based tape. Peel tests were conducted at ambient laboratory conditions at a rate of 50 mm/min (2 in./min). The universal testing machine was equipped with microcircuitry that calculated the average peel strength.

Contact Angle Measurements. Contact angle measurements are made in various ways, but all essentially refer to the equilibrium of a drop of a liquid resting on a plane solid surface under the actions of three surface tensions: (1) liquid/vapor interface (γ_{lv}), (2) solid/liquid interface (γ_{sl}) and (3) solid/vapor interface (γ_{sv}). Figure 6 (in the main text) shows these interactions.

Essentially the use of contact angle in assessing wettability reduces to the fact that contact angle is a measure of the tendency for a given mass of liquid to spread and adhere to a solid; the smaller the contact angle, the greater the spreading tendency. Since contact angle measurement is very sensitive to the first 0.5-1 nm (5-10 Å) layer on the solid surface, its behavior reflects the composition of the very top layer of the surface.

Contact angles of a polar liquid (deionized, distilled water) and a nonpolar liquid (reagent grade methylene iodide) on cleaned and uncleaned, aged EPDM rubbers were measured using a goniometer. The goniometer was equipped with an eyepiece and a protractor that allow contact angles to be measured to within 0.5 degrees. A chromatograph microsyringe was used to place a droplet of 5 µl on the surface of the specimens. Preliminary experimentation indicated that the contact angles of water on "dirty" EPDM rubber surface decreased as a function of time after the droplets were placed on the specimen surface. For that reason, in this experiment, all contact angles were taken exactly 1 minute after the droplets were placed on the surface. Four contact angle values from droplets placed at four different locations on a 1 x 6 in. (25 x 150 mm) specimen were obtained for each liquid. As indicated earlier, one specimen taken from each of the two sets was used for contact angle measurement. Thus, for each surface preparation method, the value of contact angle of each liquid was the average of eight measurements.

Wettability parameters based on contact angle measurements (i.e., polarity, polar and nonpolar [dispersion] components), and total surface free energies of the cleaned and uncleaned EPDM rubber surfaces were also calculated using the harmonic mean equation.³¹

$$\gamma_{lv} (1 + \cos\theta) = \frac{4\gamma_l^d \gamma_s^d}{\gamma_l^d + \gamma_s^d} + \frac{4\gamma_l^p \gamma_s^p}{\gamma_l^p + \gamma_s^p} \quad [\text{Eq B1}]$$

where θ is the contact angle, γ_l^d and γ_l^p are the nonpolar and polar surface free energy components of the liquid, and γ_s^d and γ_s^p are the nonpolar and polar surface free energy components of the substrate. The polarity is the ratio between the polar component and the total surface free energy. The latter is the sum of γ^d and γ^p . γ_l^d and γ_l^p values were derived by substituting into the above equation the γ^d and γ^p values of water and methylene iodide, which were taken from the literature,³² and the measured contact angles of these two liquids on each specimen surface.

Fourier Transform Infrared Spectroscopic Measurements.

Preliminary experimentation indicated that, for highly carbon- black-filled EPDM, Fourier transform infrared spectroscopy in the attenuated total reflection (FTIR-ATR) mode using single reflection produced the highest quality spectra. For that reason, unless otherwise stated, single reflection FTIR-ATR was used in this study. FTIR ATR was carried out using an FTIR spectrometer and a single reflection ATR accessory. The sections, 15x15 mm, for FTIR-ATR analysis were cut from the same cleaned EPDM rubber strips used for SEM analysis. The surface of the specimen was pressed against a ZnSe ATR prism and the contact between the specimen and the prism was controlled by a mechanical device. Care was taken to ensure that approximately the same pressure was applied for all specimens. All spectra were taken at 4 cm^{-1} resolution using 100 scans and at an incident angle of 45 degrees. In the case of the cleaned, aged EPDM rubber, the FTIR-ATR spectrum was obtained using two reflections and a KRS-5 prism plate.

The FTIR spectrum of the contaminants, removed from the aged EPDM rubber surface using a spatula, was obtained using conventional transmission spectroscopy. A 1-mm thick KBr pellet was made and the spectrum was obtained using 16 scans and 4 cm^{-1} resolution.

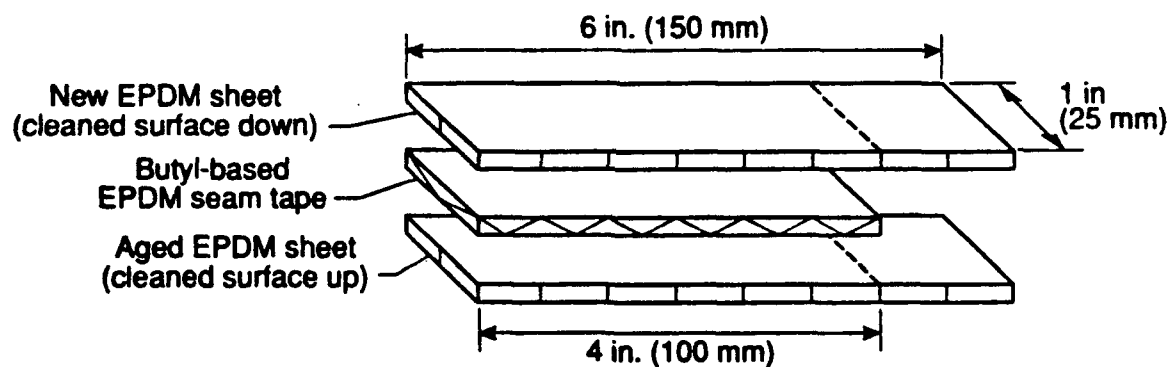
Scanning Electron Microscopy (SEM) Analysis. The sections for SEM analysis were cut from the cleaned rubber strips squares having about 8 to 10 mm (0.3 to 0.4 in.) sides. The cut pieces were adhered to SEM specimen mounting stubs with an epoxy adhesive. The mounted specimens were sputter coated with a nominal 20 nm (8×10^{-7} in.) gold conductive film to prevent surface electron charging during SEM analysis. The surfaces were examined in the SEM using an acceleration voltage of 10 kV at magnifications from x20 to x1000. Photographs were generally taken at x100 and x500 magnifications.

Creep-Rupture Tests. Creep-rupture tests were conducted according to the procedure described by Martin et al.³³ Figure B2 illustrates the seam specimen configuration. Butyl-based tape, having dimensions of 25 x 100 mm (1 x 4 in.), was adhered between the cleaned surface of the aged EPDM rubber strip and that of a new (unaged) EPDM strip. The resulting specimen was placed in a laboratory press at 1.4 MPa (200 lbf/in.²) for 5 minutes, whereafter it was kept at ambient laboratory conditions (about 22°C or 72°F and 45-50 percent relative humidity) for 7 days.

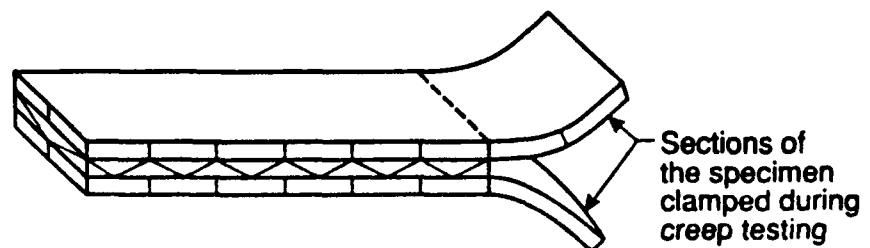
For the given cleaning method, 14 replicate peel specimens were placed under a load of 4.2 N (0.94 lbf) at a temperature of $22 \pm 1^\circ\text{C}$ ($72 \pm 2^\circ\text{F}$) and a relative humidity of $45 \pm 5\%$. The times under load over which the seam specimens completely separated were monitored electronically for each specimen. The separation caused deactivation of the electronic clock assigned to the specimen, and the recording of the time to failure.³⁴ The accuracy of the times to failure was within 1 second.

³³ Jonathan W. Martin et al., May 1990.

³⁴ Jonathan W. Martin et al., May 1990.



A. Exploded View of the Test Specimen



B. View of the Completed Test Specimen

Figure B2. Configuration of the Test Specimen Used for the Long-Term Creep-Rupture Measurements.

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